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ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XV.—OXIDATION OF β -CYMENESULPHAMIDE.

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By the oxidation of paradiethyl-sulphamide it has been shown¹ that the group C_6H_5 is protected from the action of chromic acid by the presence of the sulphamide group. Continuing the same line of investigation, the next question to be answered was whether the complex group C_6H_4 can be, in the same way, fully protected from oxidation. We may here again refer² to the highly unsatisfactory experiments of von Gerichten³ on this subject, which do not enable us to draw a definite conclusion. One of us working with L. B. Hall⁴ has proved that when the sulphamide of ordinary cymene, which is known to have the sulphamide group in the ortho position relatively to methyl, and in the meta position relatively to propyl, as expressed in the formula,⁵ $C_6H_3 \left\{ \begin{array}{l} CH_3 \\ SO_2NH_2(o) \\ C_3H_7(p) \end{array} \right.$ is oxidised with

¹ Remsen and Noyes, this Journal, **4**, 197.

² For fuller reference see *loc. cit.*

³ Berichte der deutschen chemischen Gesellschaft, **11**, 1586.

⁴ Remsen and Hall, this Journal.

⁵ Formulas of this kind have one great advantage over those in common use. They involve no hypothesis whatever regarding the structure of benzene. If, instead of the letters (*o*), (*p*), we use the figures (1), (3), we at once commit ourselves to some particular scheme for the representation of benzene. To say that two groups are in the ortho position to each other is quite a

chromic acid, the methyl is protected and the propyl converted into carboxyl. What now will be the conduct of the isomeric β -cymenesulphamide in which the sulphamide group is ortho rela-

tively to the propyl as expressed thus: $\text{C}_6\text{H}_3 \begin{cases} \text{C}_3\text{H}_7 \\ \text{SO}_2\text{NH}_2 \text{ (}o\text{)} \\ \text{CH}_3 \text{ (}p\text{)} \end{cases}$? In

order to prepare this compound we started from cymene, introduced successively bromine and the sulphonic acid group, then extracted the bromine by means of nascent hydrogen, and converted the acid thus obtained into the corresponding sulphamide. This proved to be the β -compound as we had hoped. The amide was oxidised with chromic acid and was found to conduct itself towards chromic acid quite differently from the α -compound, the entire propyl group being protected, as had seemed at least probable.

Bromcymene-sulphonic Acid.

Monobromcymene was prepared according to the directions given by Landolph.¹ A little more than the required quantity of bromine was added drop by drop to the cymene. The hydrocarbon contained a few grams (4 to 5) of iodine in solution, and the retort was placed in cold water. After all the bromine had been added, the product in the retort was heated on a water-bath for some time, and a current of air was forced through the liquid to drive out, as far as possible, the hydrobromic acid and any free bromine which might be left. After treating the contents of the retort with sodium carbonate and afterwards with a little caustic soda, the product was distilled with water vapor and subjected to fractional distillation. In the vessel in which the

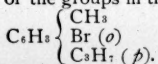
different thing from saying that the two groups are in the positions 1, 2; and the former statement is very much to be preferred. We can determine by experimental methods whether two groups are in the ortho position to each other or not, but we cannot determine whether they are in the positions 1, 2. It would be a gain if chemists would accustom themselves to use consistently such formulas as that given above. The principle, as is plain, is simply this: Let any one of the substituting atoms or groups serve as a starting-point and refer the others which may be present to this starting-point by means of the letters (*o*), (*m*) and (*p*). In some cases it will be necessary to refer a group to two others to accurately represent its relations. It is then only necessary to add a second letter indicating the relation between the group thus marked and the

one above it in the formula. Thus (I) $\text{C}_6\text{H}_2 \begin{cases} \text{CH}_3 \\ \text{Br (}o\text{)} \\ \text{SO}_2\text{OH (}m\text{) (}o\text{)} \\ \text{C}_3\text{H}_7 \text{ (}p\text{)} \end{cases}$ and (II) $\text{C}_6\text{H}_2 \begin{cases} \text{CH}_3 \\ \text{Br (}o\text{)} \\ \text{SO}_2\text{OH (}m\text{) (}p\text{)} \\ \text{C}_3\text{H}_7 \text{ (}p\text{)} \end{cases}$ represent two isomeric bromcymenesulphonic acids. In (I) the sulphonic acid group is in the meta position relatively to methyl and ortho to bromine. In (II) the same group is meta to methyl, but para to bromine. Its relation to bromine is different in the two compounds, but its relations to methyl and propyl are the same.

I. R.

¹ Berichte der deutschen chemischen Gesellschaft, 5, 267.

distillation with water was carried on there remained behind a comparatively small quantity of a non-volatile, black, gummy mass, the nature of which was not determined. That which came over with the water was mainly bromcymene, which was obtained pure after a few distillations. The vapor is irritating to the eyes and nose. When perfectly pure it is colorless, but, on standing for a time, it becomes slightly colored. Its boiling point was found to be $228-229^{\circ}$ (uncorrected) and 237° (corrected). In all we obtained about 800 grams of pure bromcymene from 1200 grams of cymene. It has been shown by von Gerichten¹ that the relations of the groups in this compound are expressed by the formula



Monobromcymene was converted into the sulphonic acid by treating it with a mixture of ordinary concentrated sulphuric and fuming sulphuric acids. The former is not strong enough and the latter may be so strong as to char the substance. By adding the mixture cautiously and preventing the reaction from becoming too violent, perfect solution of the bromcymene can be effected, and when this solution remains clear after dilution with water the transformation is complete. The sulphuric acid solution solidifies on cooling, and consists then of a mass of crystals which have a dark purple color. On diluting with water to a sufficient extent the mass is easily dissolved. This solution was neutralised with chalk, filtered and evaporated to crystallisation. The principal product obtained in this way is a calcium salt which crystallises in long beautiful needles. It is easily soluble in hot water and much less in cold. Another salt was obtained from the last mother-liquors. This could not be obtained in crystallised form, the solution forming a thick, gummy syrup. This salt and corresponding acid have not been studied as yet. It formed but a very small proportion of the entire product.

The analyses of the well-crystallised calcium salt gave the following results:

I.	0.4790	gram salt	lost	0.1069	gram H_2O	at 135°
II.	0.4139	"	"	0.0894	"	" 125°
III.	0.3187	"	"	0.0685	"	" 125°
IV.	0.5028	"	"	0.1055	"	" 135°

¹ Berichte der deutschen chemischen Gesellschaft, **11**, 1586.

V. 0.4299 gram salt dried at 175° gave 0.09385 gram CaSO_4 .

VI. 0.3973 gram dried salt gave 0.0874 gram CaSO_4 .

Calculated for $(\text{C}_{10}\text{H}_{13}\text{BrSO}_3)_2\text{Ca} + 9\frac{1}{2}\text{H}_2\text{O}$.		Found.			
		I.	II.	III.	IV.
H_2O	21.51	21.50	21.62	21.49	20.98

Calculated for $(\text{C}_{10}\text{H}_{13}\text{BrSO}_3)_2\text{Ca}$.		Found.	
		I.	II.
Ca	6.41	6.42	6.46

Barium bromcymenesulphonate, $(\text{C}_{10}\text{H}_{13}\text{BrSO}_3)_2\text{Ba} + 9\frac{1}{2}\text{H}_2\text{O}$. The free acid was prepared from the calcium salt by exactly precipitating the calcium from the solution by means of sulphuric acid. The acid was neutralised by boiling with pure barium carbonate. The salt is readily soluble in hot water, but less in cold. It crystallises like the calcium salt in long beautiful needles. It readily loses some of its water of crystallisation when exposed to the air, and hence the results of the determinations of water do not agree well with each other. In analysis I the salt was used as soon after removal from the solution as possible. In the other cases there were intervals of greater or less length between the time of exposure of the salt to the air, and that of the analysis.

I. 0.7063 gram salt lost 0.1334 gram H_2O at 130° ; and gave 0.1845 gram BaSO_4 .

II. 0.4366 gram salt lost 0.0492 gram H_2O at 130° ; and gave 0.1246 gram BaSO_4 .

III. 0.5311 gram salt lost 0.0334 gram H_2O at 145° ; and gave 0.1590 gram BaSO_4 .

IV. 0.4490 gram salt lost 0.0457 gram H_2O by standing one day in a calcium chloride desiccator, and 0.0306 gram more when heated to 145° , making a total loss in weight of 0.0763 gram; and gave 0.1203 gram BaSO_4 .

V. 0.3727 gram salt lost 0.0549 gram H_2O at 120° ; and gave 0.1013 gram BaSO_4 .

VI. 0.3544 gram salt lost 0.0542 gram at 125° ; and gave 0.0969 gram BaSO_4 .

Calculated for $(\text{C}_{10}\text{H}_{13}\text{BrSO}_3)_2\text{Ba} + 9\frac{1}{2}\text{H}_2\text{O}$.		Found.					
		I.	II.	III.	IV.	V.	VI.
H_2O	19.17	18.88	11.26	6.28	16.99	14.73	15.29

The salt with $8\text{H}_2\text{O}$ requires 16.65 per cent.; that with $7\frac{1}{2}\text{H}_2\text{O}$, 15.77 per cent.; $7\text{H}_2\text{O}$, 14.88 per cent.; $5\text{H}_2\text{O}$, 11.10 per cent.; $3\text{H}_2\text{O}$, 6.96 per cent.

Calculated for (C ₁₀ H ₁₂ BrSO ₃) ₂ Ba.	Found.					
	I.	II.	III.	IV.	V.	VI.
Ba	18.93	18.91	18.78	18.97	18.75	18.97

Zinc bromcymenesulphonate, (C₁₀H₁₂BrSO₃)₂Zn + 8H₂O. This salt was obtained from the barium salt by double decomposition with zinc sulphate. It crystallises readily in long needles. It is easily soluble in hot water; less so in cold.

I. 0.3128 gram salt lost 0.0567 gram H₂O at 150°.

Calculated for (C ₁₀ H ₁₂ BrSO ₃) ₂ Zn + 8H ₂ O.		Found.
H ₂ O	18.16	18.12

Magnesium bromcymenesulphonate (C₁₀H₁₂BrSO₃)₂Mg + 9½H₂O. This was obtained from the barium salt by double decomposition with magnesium sulphate. Its properties are like those of the salts above described. It crystallises in long needles and is easily soluble in hot water; less in cold.

I. 0.3498 gram salt lost 0.0769 gram H₂O at 145°; and gave 0.0477 gram MgSO₄.

II. 0.6225 gram salt lost 0.1357 gram H₂O at 155°; and gave 0.0944 gram MgSO₄.

Calculated for (C ₁₀ H ₁₂ BrSO ₃) ₂ Mg + 9½H ₂ O.	Found.	
	I.	II.
H ₂ O	21.98	21.79

Calculated for (C ₁₀ H ₁₂ BrSO ₃) ₂ Mg.	Found.	
	I.	II.
Mg	3.49	3.88

Sodium bromcymenesulphonate, C₁₀H₁₂BrSO₃Na + 4½H₂O. The barium was precipitated by means of sodium carbonate from a solution of barium bromcymenesulphonate. The sodium salt thus obtained crystallises in fine needles, and is easily soluble in hot and cold water.

0.305 gram salt lost 0.0604 gram H₂O at 135°; and gave 0.0528 gram Na₂SO₄.

Calculated for C ₁₀ H ₁₂ BrSO ₃ Na + 4½H ₂ O.		Found.
H ₂ O	20.46	19.80
Calculated for C ₁₀ H ₁₂ BrSO ₃ Na.		Found.
Na	7.30	6.99

The *nickel salt* was prepared by treating a solution of the barium salt with nickel sulphate. It is easily soluble and crystallises in fine needles of a delicate green color.

Bromcymenesulphamide, $C_{10}H_{12}BrSO_2NH_2$, was prepared in the usual way from the sodium salt. It is only slightly soluble in hot water and is practically insoluble in cold water. It dissolves readily in alcohol and crystallises from a mixture of alcohol and water in fine needles. The fusing point was found to be 192° (uncorrected) and 197° (corrected).

Estimations of sulphur were made by the method of Liebig, and also by that of Fahlberg and Iles. When the Liebig method was used, the first precipitate of barium sulphate obtained was dissolved in sulphuric acid and reprecipitated.

I.	0.2076 gram amide gave 0.17168 gram $BaSO_4$.
II.	0.1933 " " 0.1557 "
III.	0.1973 " " 0.1652 "
IV.	0.1553 " " 0.1272 "

Calculated for
 $C_{10}H_{14}SO_2NBr$.

S 10.95

Found.

I.	II.	III.	IV.
11.35	11.05	11.50	11.24

Bromcymenesulphonic acid has been previously prepared by Paterno and Colombo¹ and by Paterno and Canzoneri.² The former state that, when bromcymene is treated with a mixture of concentrated and fuming sulphuric acids at 100° , two crystallised sulphonic acids are formed, and that it is difficult to separate them. The latter made the acids by heating bromcymene with sulphuryl chloride, under which circumstances there are formed a bromcymenesulpho-chloride and a second bromcymenesulphonic acid which passes into solution. The amide of the acid fused at 191° , and was hence probably identical with the one obtained by us. We experienced no difficulty whatever in obtaining the main acid in pure condition and in large quantity.

β -Cymenesulphamide.

In order to replace the bromine of the bromcymene-sulphonic acid by hydrogen, a solution of the sodium salt was treated with sodium amalgam. The solution was placed in large evaporating

¹ Gazzetta chimica Italiana, **7**, 421.

² Ibid. **11**, 124; and Berichte der deutschen chemischen Gesellschaft, **14**, 1288.

dishes and kept liberally supplied with amalgam containing from 1.5 to 3 per cent. of sodium. The complete replacement required about two weeks for each solution containing 100 grams of the salt. The end of the operation was detected by acidifying a small portion of the solution with nitric acid and exactly precipitating the bromide with silver nitrate. The filtrate from silver bromide was evaporated to dryness and heated with pure lime. If no bromine was found by dissolving in nitric acid and adding silver nitrate, the strongly alkaline solution was neutralised with sulphuric acid, and the sodium sulphate separated as completely as possible by crystallisation. When no more sodium sulphate could thus be obtained the mother-liquors were evaporated to dryness. The residue was pulverised and heated for some time in an air-bath at 110° , then treated with an equal weight of phosphorus pentachloride. It was found to be necessary to slightly heat the mixture of salt and phosphorus pentachloride in order to complete the reaction. The mass became semi-liquid and towards the end of the operation free bromine was given off from the sodium bromide. Then the whole became nearly dry and colorless, when the reaction was complete. After cooling, the mass was treated with concentrated aqueous ammonia and allowed to remain in contact with it for ten or twelve hours. At the end of this time the solution was filtered from the amide, and the ammoniacal filtrate neutralised with hydrochloric acid, which caused the precipitation of a small quantity of dissolved amide.

To purify the amide it was first washed thoroughly with cold water, then dissolved in alcohol and decolorised by means of bone black. It usually contains a small quantity of a yellowish colored substance which has a low fusing point. If the amide is heated with water the colored impurity sinks to the bottom as an oil while the amide itself rises to the top of the water. By now adding alcohol cautiously the amide can be brought into solution, while the oily substance remains undissolved. From the solution in alcohol and water the amide crystallises, on cooling, in glistening scales. It is insoluble in cold water and to only a very slight extent in boiling water. It is very easily soluble in hot alcohol, and crystallises from the concentrated solution on cooling. It fuses when perfectly pure at 148° (uncorrected) and 151° (corrected). It was carefully tested for bromine and found to be entirely free from it. Estimations of sulphur and nitrogen were made with the results given below.

The first two analyses were made by Liebig's method, no special precaution being taken to remove dissolved silver. In the remaining analyses the presence of silver was prevented by a method which will be referred to in the following article.

I.	0.1642	gram amide gave 0.181	gram BaSO ₄ .
II.	0.24945	" "	0.2812 "
III.	0.3569	" "	0.3916 "
IV.	0.2138	" "	0.2304 "
V.	0.2824	" "	0.3045 "

Calculated for C ₁₀ H ₁₃ Br.SO ₂ NH ₂ .		Found.				
		I.	II.	III.	IV.	V.
S	15.02	15.13	15.47	15.06	14.79	14.80

The nitrogen estimations were made by the absolute method, the tube being exhausted by means of a Sprengel pump of the extremely convenient form suggested by Johnson and Jenkins.¹

I. 0.1911 gram amide gave 11.6 cc. nitrogen at 18.8° and 759.5 mm.

II. 0.3058 gram amide gave 19 cc. nitrogen at 20° and 756 mm.

Calculated for C ₁₀ H ₁₃ Br.SO ₂ NH ₂ .		Found.	
N		I.	II.
	6.57	6.97	7.07

The amide obtained by us has then the composition of cymene-sulphamide, and the reactions made use of are of such a kind that it is difficult to see how they could have caused a molecular rearrangement. The amide is plainly quite a different substance from α -cymenesulphamide. This has been thoroughly studied and its properties are well known. It fuses at 113–114°. As, according to the commonly accepted hypothesis, there can be but two sulphamide derivatives of paracymene, represented respectively by the formulas (I) $\text{C}_6\text{H}_3 \begin{Bmatrix} \text{CH}_3 \\ \text{SO}_2\text{NH}_2 \text{ (} \phi \text{)} \\ \text{C}_6\text{H}_7 \text{ (} \rho \text{)} \end{Bmatrix}$ and (II) $\text{C}_6\text{H}_3 \begin{Bmatrix} \text{C}_6\text{H}_7 \\ \text{SO}_2\text{NH}_2 \text{ (} \phi \text{)} \\ \text{CH}_3 \text{ (} \rho \text{)} \end{Bmatrix}$ and as the well-known α -amide has been proved to have the formula I, it would seem to follow that our amide fusing at 147.5°–148° must be represented by formula II. We started from cymene and introduced bromine. The product is represented by

¹ This Journal, 2, 28.

the formula $C_6H_5 \begin{Bmatrix} CH_3 \\ Br (o) \\ C_3H_7 (p) \end{Bmatrix}$. Into this the sulphonic acid group was introduced. On now replacing the bromine by hydrogen the product is found to be a compound of the formula $C_6H_5 \begin{Bmatrix} C_3H_7 \\ SO_2OH (o) \\ CH_3 (p) \end{Bmatrix}$.

Hence it follows that bromcymenesulphonic acid must have the formula $C_6H_5 \begin{Bmatrix} CH_3 \\ Br (o) \\ SO_2OH (m) (p) \\ C_3H_7 (p) \end{Bmatrix}$ or $C_6H_5 \begin{Bmatrix} CH_3 \\ Br (o) \\ SO_2OH (m) (o) \\ C_3H_7 (p) \end{Bmatrix}$.

Earlier investigators have described a β -cymenesulphonic acid supposed to have the formula $C_6H_5 \begin{Bmatrix} C_3H_7 \\ SO_2OH (o) \\ CH_3 (p) \end{Bmatrix}$, but the properties of the amide obtained from this acid are not like those of our amide. Thus Claus and Cratz¹ refer to a second acid formed when cymene is treated with sulphuric acid. Later, Claus² gives directions for the preparation of β -cymenesulphonic acid. The best yield is obtained by treating one part of pure cymene with five parts of concentrated sulphuric acid for from six to eight hours on the water-bath, the mixture being frequently shaken. Several salts of the acid were prepared, as well as the chloride and amide. Of the amide he only says that it was obtained in the form of an uncrystalline oil. Either it was very impure or it was entirely different from our product. Spica³ also claims to have obtained β -cymenesulphonic acid, but if his statement is correct that the amide of the acid fuses at 73.5° – 74° , then it is clear that his product was not identical with ours. According to later statements by Spica⁴ and by Claus⁵ it seems possible that the amide first obtained by Spica and described by him as β -cymenesulphamide is in reality a derivative of metacymene, which, according to Spica,⁶ is contained in cymene from camphor.

Notwithstanding the fact that our amide has the composition of cymenesulphamide and was prepared by reactions which can leave little doubt in regard to its nature, it must be considered an open question whether it is really β -cymenesulphamide. The mere fact that its properties are not the same as those of the β -cymenesulphamide of Claus is not sufficient to arouse serious doubt in our

¹ Berichte der deutschen chemischen Gesellschaft, **13**, 901.

² Ibid. **14**, 2139.

³ Ibid. 652.

⁴ Ibid. **15**, 791, and Gazzetta chimica Italiana, **12**, 482.

⁵ Berichte der deutschen chemischen Gesellschaft, **15**, 1015.

⁶ Loc. cit.

minds concerning its nature, for it is quite possible that further investigation of the β -cymenesulphonic acid obtained directly from cymene may show it to yield an amide identical with ours. Other facts, however, which have been developed in the course of this investigation, and which will be more fully described in the next paper, seem to be inexplicable if our amide is really β -cymenesulphamide in which the propyl group is normal.

The transformation of the amide into thymol would be of some assistance in attempting to solve the problem.

Fusion of β -Cymenesulphamide with Potassium Hydroxide.

A few grams of β -cymene sulphamide were fused with potassium hydroxide. A dark colored oil soon separated on the surface of the fused mass, and the odor of thymol was at once perceived. This odor continued throughout the fusion, the oil disappearing very slowly. On cooling, the oil solidified and proved to be mainly unchanged sulphamide. The contents of the crucible were dissolved in water and acidified, when the odors of sulphur dioxide and of thymol became very distinct. The solution was extracted with ether and the ether distilled off. There remained behind a crystalline mass of dark color which had the unmistakable odor of thymol. It was impossible to distinguish between the odor of this substance and that of pure thymol. Nevertheless, we were unable, with the small quantity at our disposal, to isolate the pure thymol. While in our minds there is little, if any, doubt that thymol was thus obtained synthetically, we can furnish no perfectly satisfactory proof. If we consider the very strong and characteristic odor of thymol, however, it must be acknowledged that proof based upon recognition of this odor is fairly convincing.

The conversion of the sulphamide into the corresponding hydroxyl derivative does not take place very readily at a low temperature, and, if the temperature be raised much higher, deeper decomposition takes place. We hope to return to this subject at some future time.

Oxidation of β -Cymenesulphamide.

The best proportions for the oxidation of the amide we have found to be: 5 grams amide to 25 grams potassium pyrochromate,

40 grams concentrated sulphuric acid diluted with three times its volume of water. The mixture was boiled for six hours in a flask connected with an inverted condenser. After cooling, the contents of the flask were diluted with water, filtered and washed until the wash-water passed through colorless. The white crystalline acid upon the filter was dissolved in a dilute solution of sodium carbonate. The solution was filtered and allowed to stand, when some unchanged amide crystallised out. On adding hydrochloric acid a precipitate was formed, which after filtering and washing was converted into the barium salt. This is extremely soluble. Its solution was evaporated down to a small volume and allowed to stand, when a small quantity of unchanged amide again separated. The acid was set free, washed, filtered, crystallised from water, and again converted into the barium salt. This process was repeated several times, as it was extremely difficult to completely remove the small quantity of amide. Finally, however, the acid was obtained in perfectly pure form. It is comparatively easily soluble in hot water, and crystallises, on cooling, in the form of beautiful, long needles. It fuses at 232° (uncorrected) and 244° (corrected). Sulphur and nitrogen estimations were made with the following results:

I. 0.2344 gram substance gave 0.227 gram BaSO_4 .

II. 0.4164 gram substance gave 23 cc. nitrogen. Temperature $30^{\circ}\text{C}.$; pressure 758 mm. Absolute method with mercury pump.

Calculated for $\text{C}_{10}\text{H}_{13}\text{O}_4\text{SN}.$

S	13.17
N	5.76

Found.

13.30
5.98

Analyses of the barium salt were also made. Analyses (I), (II), (III) and (IV) were made with specimens of the salt which we afterward found to contain small quantities of unchanged amide, and from which it was finally separated by the method described above. Analyses (V) and (VI) were made with the perfectly pure substance.

I. 0.2273 gram salt lost 0.0179 gram H_2O at 125° ; and gave 0.0767 gram BaSO_4 .

II. 0.2504 gram salt lost 0.0217 gram H_2O at 150° ; and gave 0.0842 gram BaSO_4 .

III. 0.2912 gram salt lost 0.0265 gram H_2O at 148° ; and gave 0.0973 gram BaSO_4 .

IV. 0.2410 gram salt lost 0.0219 gram H_2O at 150° ; and gave 0.0808 gram BaSO_4 .

V. 0.3173 gram salt lost 0.0198 gram H_2O at 154° ; and gave 0.1115 gram BaSO_4 .

VI. 0.4685 gram salt lost 0.0324 gram H_2O at 154° ; and gave 0.1637 gram BaSO_4 .

The results for water of crystallisation do not agree well with one another. It is probable that the first specimens analysed (I-IV) were not perfectly dry. They were poorly crystallised, while the two pure specimens (V and VI) were much better crystallised.

		Found.			
Calculated for $(\text{C}_{10}\text{H}_{13}\text{SO}_4\text{N})_2\text{Ba} + 3\text{H}_2\text{O}$.		I.	II.	III.	IV.
H_2O	8.00	7.87	8.66	9.10	9.08

		Found.	
Calculated for $(\text{C}_{10}\text{H}_{13}\text{SO}_4\text{N})_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$.		I.	II.
H_2O	6.74	6.24	6.91

		Found.					
Calculated for $(\text{C}_{10}\text{H}_{13}\text{SO}_4\text{N})_2\text{Ba}$.		I.	II.	III.	IV.	V.	VI.
Ba	22.06	21.53	21.64	21.61	21.68	22.03	22.07

Discarding the results of the first four analyses for the reasons above given, it will be seen that the agreement between the calculated and found percentages for barium is almost perfect. It follows that the acid with which we are here dealing has the composition $\text{C}_{10}\text{H}_{13}\text{SO}_4\text{N}$. The amide which yields this acid by oxidation has the composition $\text{C}_{10}\text{H}_{13}\text{SO}_3\text{N}$. A methyl group is changed to

carboxyl. From the amide, $\text{C}_6\text{H}_5 \begin{cases} \text{C}_3\text{H}_7 \\ \text{SO}_2\text{NH}_2(o), \\ \text{CH}_3(p) \end{cases}$ we have ob-

tained by oxidation the acid, $\text{C}_6\text{H}_5 \begin{cases} \text{C}_3\text{H}_7 \\ \text{SO}_2\text{NH}_2(o), \text{ i. e. sulphamine-} \\ \text{CO}_2\text{H}(p) \end{cases}$

parapropylbenzoic acid. The most important point to be noted in this connection is the fact that the entire propyl group, C_3H_7 , is protected from the action of the oxidising mixture—a fact which is in perfect harmony with the views which were advanced some time ago by one of us, and the correctness of which is being more and more satisfactorily demonstrated by the investigations carried on in this laboratory. In fact, the conduct of the two cymene-sulphamides towards chromic acid furnishes the most strik-

ing illustration of the working of the law of protection. The

α -amide, $C_6H_5 \left\{ \begin{array}{l} CH_3 \\ SO_2NH_2 (o) \\ C_2H_5 (p) \end{array} \right.$, yields sulphamine-paratoluic acid,

$C_6H_5 \left\{ \begin{array}{l} CH_3 \\ SO_2NH_2 (o) \\ CO_2H (p) \end{array} \right.$. In this case, the methyl being in the ortho

position relatively to the sulphamide group, is protected, while the propyl group breaks down and yields carboxyl, exactly as if the sulphamide group were not present. In the case of the β -amide, however, as has been seen, the propyl group being now in the ortho position relatively to methyl, is protected, while the methyl is changed to carboxyl. This is certainly the simplest interpretation of the reactions which have been considered in this paper, and were it not for facts established in an investigation which was carried on by Mr. E. H. Keiser and one of us simultaneously with this, there would be no good reason for thinking that anything had taken place besides that which appears at first sight. As will be pointed out, however, it seems at least possible that the normal propyl group of cymene may have undergone a change to the isopropyl group under the influence of some of the reagents used. It would, however, be premature to discuss this possibility without having first considered the unexpected facts which have suggested it.

Whether the group in our amide be normal propyl or isopropyl, and this is the only question in regard to the compound which can be considered open, the fact remains that the entire group is protected, and the main object in view as well as the result obtained are not in the least affected by the possible transformation.

XVI.—OXIDATION OF PARA-DIPROPYL-BENZENE-SULPHAMIDE.

BY IRA REMSEN AND E. H. KEISER.

The object of this investigation was like that of the one just described—to determine whether an acid group in the ortho position relatively to propyl has the power to protect this group from the oxidising action of chromic acid. In this case we started from paradipropylbenzene, introducing into it the sulphonic acid group and transforming the acid into the corresponding amide. According to all that we know of the compound thus prepared, it must

contain the sulphamide group in the ortho position relatively to one propyl group, and in the meta position relatively to the other. In the light of the results described in the preceding paper we would expect such a compound to yield by oxidation a sulphamine-parapropyl-benzoic acid identical with the one described above. As will be seen, an acid of the composition of a sulphamine-parapropyl-benzoic acid was actually obtained in this case as well as the other; but, strange to say, the two have quite different properties.

Paradiethylbenzene was prepared according to the directions given by Körner.¹ Eighteen flasks of 125 cc. capacity were charged each with 25 grams paradiethylbenzene, 39 grams propyl bromide (from Kahlbaum, boiling point 71°), 14.6 grams metallic sodium cut in thin shavings, and 10 grams pure benzene. Each flask, provided with a long glass tube to serve as a condenser, was placed in a vessel containing cold water and allowed to stand until the action seemed to be finished. To each flask there was then added 10 grams propyl bromide, after which it was heated in an oil bath for two hours at 120° . To prevent loss there was attached a condenser with a mercury valve. The flask was then heated over a naked flame and everything volatile distilled off. The distillate thus obtained was fractioned and the diethylbenzene easily obtained in pure condition. From the eighteen flasks, containing 450 grams diethylbenzene, we obtained 86 grams of the hydrocarbon boiling between 210° and 220° . By far the greater part of this passed over at 214° (uncorrected) or 224° (corrected). Körner gives the boiling point at 220° – 222° .

Para-diethylbenzene-sulphonic Acid.

To about 75 cc. of fuming sulphuric acid 40–50 grams of the hydrocarbon were gradually added, the flask being constantly shaken. The mixture became warm at once, and the reaction was easily completed by heating the substances on a water-bath for a few minutes. After diluting, the acid was neutralised with barium carbonate. The barium salt of the sulphonic acid crystallised out of the concentrated solution in the form of minute needles, which effloresced rapidly in the air. Analyses gave the following results:

I. 0.2885 gram salt lost 0.0086 gram H_2O at 160° , and gave 0.1032 gram $BaSO_4$.

¹ *Annalen der Chemie*, **216**, 223.

II. 0.4515 gram salt lost 0.0147 gram H_2O , and gave 0.1633 gram BaSO_4 .

III. 0.1876 gram lost 0.007 gram H_2O .

Calculated for
 $(\text{C}_{12}\text{H}_{17}\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$.
 H_2O 5.49

Found.		
I.	II.	III.
2.98	3.25	3.78

Calculated for
 $(\text{C}_{12}\text{H}_{17}\text{SO}_3)_2\text{Ba}$.
Ba 22.13

Found.	
I.	II.
21.68	21.98

The barium salt was converted into the potassium salt by treatment with potassium carbonate. It crystallises in large transparent plates, which retain their transparency after the water of crystallisation is driven off.

0.3174 gram salt lost 0.0072 gram H_2O at 140° , and gave 0.0955 gram K_2SO_4 .

Calculated for $(\text{C}_{12}\text{H}_{17}\text{SO}_3)\text{K} + 4\text{H}_2\text{O}$.
 H_2O 2.04

Found.
2.26

Calculated for $(\text{C}_{12}\text{H}_{17}\text{SO}_3)\text{K}$.
K 13.95

Found.
13.82

To convert the potassium salt into the amide it was treated in the usual way successively with phosphorus pentachloride and strong aqueous ammonia. Ammonia gas was passed into the liquid for some time to insure the perfect transformation of the chloride into the amide. The amide is difficultly soluble in boiling water; easily soluble in alcohol. When pure it fuses at 103° , and if allowed to solidify suddenly it will melt again at a lower temperature. From the alcoholic solution it may be obtained in the form of perfectly clear transparent crystals. These appear to be monoclinic prisms, and at times they reach a length of at least half an inch. Very perfect, clear rhombohedra were afterwards obtained. At our request, Dr. G. H. Williams has examined the crystals and reports as follows regarding them:

"The crystals of paradipropylsulphamide intrusted to me by Prof. Remsen for examination, though at the first glance appearing to consist of a monoclinic combination, ∞P (110) and oP (001), proved to belong to the rhombohedral division of the hexagonal system. The examination of a large number of crystals failed to reveal any other form than the fundamental rhombohedron, R, which

is generally so much elongated in the direction of one zone of combination edges as to give the crystals an acicular habit. Sometimes the rhombohedron is developed in the form of a thin plate parallel to one of the faces, and then generally has a hopper-like shape characteristic of crystals whose growth has been rapid. More rarely, among the minutest crystals, symmetrically developed rhombohedrons were observed. The crystals were all quite small, very seldom exceeding 4 mm. in length by 1 mm. in thickness.

"The average of measurements on five crystals gave for the rhombohedral angles $104^{\circ} 27' 54''$ and $75^{\circ} 29' 12''$, the agreement being as great as could be expected, considering the somewhat uneven character of the planes. The axial ratio calculated from these angles is $a : c = 1 : 0.85592$, showing a close similarity to that of calcite ($= 1 : 0.8542988$).

"In parallel polarised light all crystals extinguish parallel to the diagonals of the rhombohedral faces. In converged light a uniaxial interference figure with a large number of rings, indicating a great divergence of the two rays, as in the case of calcite, was observed. Double refraction negative.

"On account of the minuteness of the crystals, and still more on account of the extreme brittleness of the substance, it was found impossible to prepare sections perpendicular to the vertical axis or prisms for the determination of the index of refraction.

"In all crystallographic as well as optical properties the close resemblance of this substance to calcite is very striking."

Estimations of sulphur and nitrogen were made. In the sulphur estimation, which was made according to Liebig's method, special precautions were taken to remove silver from the solution. This is quite necessary in order that satisfactory results may be obtained. One of us (K.) has undertaken a study of the best conditions for the estimation of sulphur in organic compounds.¹ The results obtained are very satisfactory.

I. 0.2464 gram substance gave 0.2399 gram BaSO_4 .

II. 0.2667 gram substance gave 13.4 cc. N at 18° and 766 mm. pressure ($= 0.0156$ gram N). Absolute method with Sprengel pump.

Calculated for $\text{C}_{12}\text{H}_{19}\text{NSO}_3$.		Found.
S	13.27	13.37
N	5.81	5.85

¹ See paper on "Estimation of Sulphur in Organic Compounds" in this number.

Oxidation of Para-dipropyl-benzene-sulphamide.

The proportions used in the oxidation experiments were these: 10 grams amide, 66 grams potassium pyrochromate and 96 grams concentrated sulphuric acid diluted with three times its volume of water. The oxidising mixture was allowed to become cold before the amide was added. The whole was boiled for from eight to ten hours. Some unchanged amide still remained in the flask, and, after cooling, formed a film on the surface of the oxidising mixture, while small crystals of the oxidation product were observed in the liquid. The liquid was filtered, leaving the crystallised oxidation product on the filter, while the cake of amide remained in the flask. The oxidising mixture was returned to the flask, and the boiling started again. When the mixture had become dark green, a few grams of the pyrochromate and a little sulphuric acid were added, and the oxidation continued until, on cooling, there was seen no film of unchanged amide on the surface of the liquid. The oxidation was effected with considerably more difficulty than that of β -cymenesulphamide as described in the preceding article. The product left on the filter was washed with cold water until the wash-water passed through colorless. It was then dissolved in boiling water and filtered, when, on cooling, it crystallised out in beautiful, long, lustrous needles. After two or three crystallisations from water it was perfectly free from the original amide. It was then found to fuse at 212° – 213° (corrected). It is an acid. Its composition was determined by estimations of sulphur and nitrogen and by analyses of the barium, calcium, copper and silver salts.

The sulphur and nitrogen estimations gave the following results:

- I. 0.2599 gram gave 13.3 cc. N at 20° and 761 mm. pressure (=0.0153478 gram N). Absolute method with Sprengel pump.
- II. 0.2852 gram gave 0.2773 gram BaSO_4 .

Calculated for $\text{C}_{10}\text{H}_{12}\text{SNO}_4$.

N	5.76
S	13.17

Found.

5.90
13.35

The acid has the composition of *sulphamine-propyl-benzoic acid*, and the analyses of the salts confirm these results.

Barium sulphamine-propyl-benzoate, $(\text{C}_{10}\text{H}_{12}\text{SNO}_4)\text{Ba} \cdot x\text{H}_2\text{O}$. This salt was prepared by boiling the free acid with pure barium carbonate. It is very easily soluble and was not obtained in the

form of crystals. The solution was evaporated to dryness and the salt heated to 150° .

I. 0.0975 gram dried salt gave 0.0367 gram BaSO_4 .

II. 0.1424 gram dried salt gave 0.0533 gram BaSO_4 .

Calculated for $(\text{C}_{10}\text{H}_{12}\text{SO}_4\text{N})_2\text{Ba}$.		Found.	
		I.	II.
Ba	22.06	22.13	22.00

Calcium sulphamine-propyl-benzoate, $(\text{C}_{10}\text{H}_{12}\text{SO}_4\text{N})_2\text{Ca} \cdot 6\text{H}_2\text{O}$, was prepared like the barium salt. It is very easily soluble in water and in alcohol and could not be obtained in the form of well-defined crystals.

0.2431 gram salt lost 0.0426 gram H_2O at 140° ; and gave 0.0508 gram CaSO_4 .

Calculated for $(\text{C}_{10}\text{H}_{12}\text{SO}_4\text{N})_2\text{Ca} + 6\text{H}_2\text{O}$.		Found.
H_2O	17.09	17.52

Calculated for $(\text{C}_{10}\text{H}_{12}\text{SO}_4\text{N})_2\text{Ca}$.		Found.
Ca	7.63	7.45

Copper Salt.—When an aqueous solution of the acid is boiled with an excess of copper oxide, the solution filtered and evaporated to a small volume, a salt separates in the form of minute blue crystals which appeared to be as easily soluble in cold water as in hot. The analyses showed it to consist of a molecule of the neutral copper salt plus a molecule of the free acid. That the compound still had acid properties was shown by dissolving a little in water and testing the solution with blue litmus paper. The addition of a little sodium carbonate to it caused an evolution of carbon dioxide. The substance had a definite crystalline form and could not for a moment be regarded as a mixture. We give the analytical results and the simplest formula deducible from them, which is $(\text{C}_{10}\text{H}_{12}\text{SO}_4\text{N})_2\text{Cu} + \text{C}_{10}\text{H}_{12}\text{SO}_4\text{N} + 2\text{H}_2\text{O}$.

I. 0.2270 gram salt lost 0.0103 gram H_2O , and gave 0.0214 gram CuO .

II. 0.1970 gram salt lost 0.0093 gram H_2O , and gave 0.0188 gram CuO .

Calculated for the above formula.		Found.	
		I.	II.
H_2O	4.36	4.54	4.72

Calculated for dried salt.		Found.	
		I.	II.
Cu	7.97	7.87	7.98

Silver sulphamine-propyl-benzoate, $(C_{10}H_{13}SO_4N)Ag$, was prepared by adding silver nitrate to a solution of the neutral ammonium salt. It is thrown down as a flocculent white mass, which rapidly becomes brown if exposed to the light. The specimen analysed was kept in the dark until dry. The salt passes into solution in water if boiled for some time, but it does not crystallise from the solution, even when evaporated down to a small volume.

0.2732 gram dried salt gave a residue of metallic silver weighing 0.084 gram.

Calculated for $(C_{10}H_{13}SO_4N)Ag$.

Ag 30.86

Found.

30.75

It is clear from the analyses above quoted that the acid with which we are dealing has the composition of a sulphamine-propyl-

benzoic acid, $C_6H_5 \left\{ \begin{array}{l} C_3H_7 \\ SO_2NH_2 \\ CO_2H \end{array} \right.$. Further, as we started from para-

dipropyl-benzene, the carboxyl in the acid must be in the para position relatively to the propyl. Hence the sulphamide group must be either ortho to propyl and meta carboxyl, or ortho to carboxyl and meta to methyl. Considering the results obtained in the earlier investigations of this series, we can scarcely be in doubt regarding the relation of the groups. We can see no reason why the sulphamide group should not exert a protective action upon the ortho propyl group in this case as well as in the case of β -cymene-sulphamide. But if it does exert this action, then the product obtained by oxidising para-dipropyl-benzene-sulphamide,

$C_6H_5 \left\{ \begin{array}{l} C_3H_7 \\ SO_2NH_2 \\ C_3H_7 \end{array} \right.$ (ϕ), ought to be identical with that obtained by

oxidising β -cymene-sulphamide, $C_6H_5 \left\{ \begin{array}{l} C_3H_7 \\ SO_2NH_2 \\ CH_3 \end{array} \right.$ (ϕ). It should be

$C_6H_5 \left\{ \begin{array}{l} C_3H_7 \\ SO_2NH_2 \\ CO_2H \end{array} \right.$ (ϕ). The products obtained in the two cases are,

however, not identical in properties, though they have the same composition. The sulphamine-propyl-benzoic acid obtained from β -cymene-sulphamide, and which we will hence call the β -acid, fuses at 244° (corrected), whereas the acid described in this paper, and which may be called the α -acid, fuses at 212° - 213° (corrected). They resemble each other in appearance and in other general

properties. Between their barium salts differences could easily be detected. That of the β -acid, although very easily soluble, could be obtained in definite crystallised form, while that of the α -acid could not be obtained in crystallised form.

How shall we explain the difference between the two acids? Without further experiments this is impossible. There are two thoughts, however, which suggest themselves and indicate the lines of work, the following of which will be most likely to lead to a solution of the curious problem which is here presented. The first is this: It is possible that in the reactions made use of for the preparation of β -cymene-sulphamide there may have been a transformation of the normal propyl into the isopropyl group, so that the final product may be an isopropyl instead of a normal propyl compound. The possibility of such a transformation has been proved in a number of cases. We recall here the following, as bearing particularly upon our own work: Kekulé and Schrotter¹ found that by long boiling of normal propyl bromide with aluminium bromide, isopropyl bromide is produced. Aronstein² found that this same change is effected without the presence of aluminium bromide by simply heating to 280°. Gustavson³ has found that cymene is decomposed by bromine in the presence of aluminium chloride, yielding pentabromtoluene and *isopropyl bromide*. The same chemist has also observed⁴ that cumene (isopropylbenzene) can be obtained by the action of propyl bromide on benzene in the presence of aluminium bromide. By boiling cuminic alcohol with zinc dust, Kraut⁵ obtained cymene, isopropyl being in this case changed to normal propyl. Other transformations of normal propyl into isopropyl, or *vice versa*, have been observed by R. Meyer and H. Bauer,⁶ Jacobsen,⁷ Nencki and Ziegler,⁸ Ziegler,⁹ and Paterno and Spica.¹⁰ Whether such a transformation has taken place in either of the cases under immediate consideration can probably be decided by starting from para-isopropylbenzene and performing the same experiments as those which have been described in this paper. The product of the oxidation of the sulphamide should be identical either with the α - or the β -acid.

The second thought which has suggested itself by way of expla-

¹ Berichte der deutschen chemischen Gesellschaft, 12, 2279.

² Ibid. 14, 607; and Recueil des Travaux chimiques des Pays Bas, 1, 134.

³ Berichte der deutschen chemischen Gesellschaft, 10, 1101.

⁴ Ibid. 11, 1251.

⁵ Ibid. 11, 1379.

⁶ Ibid. 14, 1135.

⁷ Ibid. 12, 429 and 1512.

⁸ Ibid. 5, 749.

⁹ Ibid. 14, 1144.

¹⁰ Ibid. 12, 2366.

nation of the facts with which we are dealing is that, in the preparation of β -cymene-sulphonic acid by treating bromcymenesulphonic acid with sodium amalgam, some of the nascent hydrogen may have been added to the compound, and that the product really obtained was not cymene-sulphonic acid but a hydrogen addition product. As is well known, the action of sodium amalgam in alkaline solution is made use of for the purpose of making dihydrophthalic and dihydroterephthalic acids. The presence of the two hydrogen atoms in the cymenesulphamide and in the acid obtained from it could hardly be detected with certainty by analyses. On the other hand, the great stability of β -sulphamine-propyl-benzoic acid towards the chromic acid mixture would seem to be an argument against the view that the acid is a hydrogen addition product.

An experiment was made in the hope of throwing some light on the question by treating the α -sulphamine-propyl-benzoic acid with sodium amalgam in alkaline solution. It was thought possible that in this way the α -acid might be converted into the β -acid. The experiment led to no positive results. We had only half a gram of substance at our disposal. This was dissolved in caustic soda, and the solution kept supplied with sodium amalgam for about three weeks. For some reason, however, we were unable to recover any of the acid unchanged, nor could we isolate any difficultly soluble substance from the solution.

As we had found the sulphamide of dipropyl-benzene to resist the action of chromic acid very markedly, it was necessary to show that, when dipropyl-benzene itself is oxidised, both propyl groups are changed to carboxyl. For this purpose, 5 grams of the hydrocarbon were treated with 33 grams potassium pyrochromate and 48 grams of sulphuric acid diluted in the usual way. The mixture was kept boiling for several hours, when the unoxidised hydrocarbon was distilled off with water. The residue was filtered, and in the filter there was collected a considerable quantity of a white insoluble powder. This was dissolved in ammonia and precipitated by means of hydrochloric acid. After drying, an attempt was made to determine its fusing point. It was found, however, that it sublimed without fusing. Its conduct showed beyond a question that it was terephthalic acid.

Finally, the oxidising mixtures filtered off from α -sulphamine-propyl-benzoic acid were evaporated down. After standing for

some time a small quantity of minute white crystals separated. These were filtered off and recrystallised from water containing hydrochloric acid. They proved to be a potassium salt. When pure, the salt crystallised in needles.

The analyses gave the following results :

0.1702 gram lost 0.0063 gram H_2O , and gave 0.05 gram K_2SO_4 .

These results correspond to 3.70 per cent. H_2O and 13.68 per cent. K. The salts $C_6H_5 \begin{cases} C_6H_5 \\ SO_2OK \\ CO_2H \end{cases}$ and $C_6H_5 \begin{cases} CO_2H \\ SO_2OK \\ CO_2H \end{cases}$ contain

almost identically the same percentages of potassium, there being a difference of only two in the molecular weights of the two substances. A neutralisation experiment showed, however, that the salt under examination still contains two replaceable hydrogen atoms.

0.1737 gram salt dried at 240° lost 0.0072 gram H_2O , and then required for neutralisation 0.02008 gram ammonia. If it had been the salt with one carboxyl it would have required 0.01003 gram ammonia, while if it is the substance $C_6H_5 \begin{cases} CO_2H \\ SO_2OK \\ CO_2H \end{cases}$, it would require 0.01993 gram ammonia.

Calculated for $C_6H_5 \begin{cases} CO_2H \\ SO_2K \\ CO_2H \end{cases} + \frac{1}{2}H_2O$,
 $\frac{1}{2}H_2O$ 3.10

Calculated for anhydrous salt,
 K 13.76

Found.	
I.	II.
4.14	3.70

Found,
 13.68

The substance is therefore *mono-potassium sulphoterephthalate*, and it has been formed by further oxidation of either sulphopropylbenzoic or sulphamine-propylbenzoic acid. The results obtained in estimating the water of crystallisation are not satisfactory, more than one per cent. too much having been found in the first analysis. A mono-potassium sulphoterephthalate has already been described by Remsen and Hall¹ and Remsen and Burney.² The properties of the substance obtained in this investigation are apparently the same as those previously ascribed to the salt. The only difference is in the water of crystallisation. In the earlier investigations the crystallised salt was found to contain one molecule of water. Now, however, although more than half a

¹ This Journal, 2, 56.

² Ibid. 2, 412.

molecule is found, there is not as much as there ought to be. We are at present unable to explain this discrepancy.

It is clear then that when para-dipropyl-benzene-sulphamide is oxidised by means of chromic acid, the principal product is the acid which we have called α -sulphamine-propyl-benzoic acid, the formation of which under the conditions described proves that the sulphamide group exerts a protective action upon one of the propyl groups. At the same time the protection is not perfect, as has been shown in other cases, and as is shown in this case by the formation of sulpho-terephthalic acid. In oxidising α -metaxylene-sulphamide with chromic acid Remsen and Iles¹ observed a similar formation of a small quantity of sulpho-isophthalic acid.

SYNTHETICAL RESEARCHES IN THE GLUCOSIDE GROUP.²

II.

BY ARTHUR MICHAEL.

Action of Acetic Anhydride on Phenolglucoside.

The action of acetochlorhydrose on an alcoholic solution of sodium phenyl oxide unexpectedly gave phenolglucoside, instead of the tetra-acetyl derivative of that compound. This result seemed to indicate that the tetra-acetyl compound would be decomposed in the cold by alcohol into ethyl acetate and the glucoside. The formation of helicin from acetochlorhydrose and sodium salicylaldehyde, however, showed that this conclusion can hardly be accepted, since tetra-acetyl helicin, once formed, is but slightly decomposed by alcohol, even on boiling.³ The following experiments show that the acetyl derivative of phenolglucoside is also stable towards alcohol. To prepare the acetyl compound, a mixture of 1 part of phenolglucoside, 5 parts of acetic anhydride and 2 parts of fused sodium acetate was heated for about three hours in a hot water-bath. The product of the reaction was poured into cold water, allowed to stand for several hours, then slightly warmed and, after

¹ This Journal, 1, 121.

² See this Journal, 1, 304.

³ Annalen der Chemie, 154, 23.

cooling, filtered. The crystalline, insoluble residue was purified by two crystallisations from alcohol. On analysis the following numbers were obtained:

0.2255 gram of substance, dried at 100° , gave 0.4693 gram of CO_2 and 0.121 gram of H_2O .

Theory for $\text{C}_8\text{H}_7\text{O}(\text{OC}_6\text{H}_5)(\text{OC}_2\text{H}_5\text{O})_4$.		Found.
C	56.60	56.75
H	5.66	5.96

Tetra-acetylphenolglucoside crystallises from alcohol in white, glittering, long needles. It is insoluble in cold, but slightly in hot water. Cold alcohol dissolves it slightly, warm very readily. Heated with caustic soda it is decomposed into sodium acetate, sodium phenyl oxide and brown decomposition products of dextrose. It may be crystallised from hot alcohol without undergoing any noticeable decomposition. If the alcoholic solution is boiled for several minutes, the odor of ethyl acetate is noticeable. The decomposition is however very slight, for an alcoholic solution heated for an hour in a flask connected with an inverted cooler gave on cooling almost the original amount of the acetyl compound. The substance does not reduce a solution of potassium copper tartrate, except after long boiling; a reduction doubtless owing to the previous formation of dextrose.

Synthesis of Salicin from synthetical Helicin.

N. Lisenko¹ has shown that helicin obtained from salicin can be reconverted into the latter compound by treating an aqueous solution of it with sodium amalgam. This, according to H. Schiff,² can also be effected by using zinc and sulphuric acid. I deemed the repetition of this experiment, using helicin obtained from acetchlorhydrose and sodium salicylaldehyde, of some interest.

The directions given by Lisenko were closely followed. The aqueous solution was treated with sodium amalgam, and care was taken to keep the solution but slightly alkaline. The filtrate from the mercury was neutralised by carbonic acid, evaporated to dryness on a water-bath, and the residue extracted with hot alcohol. The reduction product was purified by several crystallisations from water. An analysis gave the following numbers:

¹ Zeitschrift für Chemie, 1864, 577.

² Annalen der Chemie, 154, 26.

0.1858 gram of substance gave 0.3706 gram of CO_2 and 0.1077 gram of H_2O .

Theory for $\text{C}_8\text{H}_{11}\text{O}_6-\text{O}-\text{C}_6\text{H}_4\text{CH}_2\text{OH}$.		Found.
C	54.54	54.39
H	6.29	6.44

The properties of the compound confirm the conclusion that may be drawn from the analysis. They agree perfectly with those of natural salicin. This is the first known instance of a synthesis of a glucoside occurring in nature.

Action of Acetochlorhydrose on Dipotassium Salicylate.

Tiemann and Reimer¹ have examined the action of potassium permanganate on salicin with a view of converting the formyl of the salicylaldehyde radical into carboxyl. The alkaline solution of the oxidation product did not change Fehling's solution, even on boiling, nor was salicylic acid precipitated on the addition of acids. If, however, the acidified solution was gently heated, on cooling salicylic acid was precipitated. This result indicated that the glucoside of salicylic acid was formed, but it was found impossible to isolate the compound in a pure state. It seemed possible to obtain this compound by the action of acetochlorhydrose on dipotassium salicylate. The investigation of the reaction gave an unexpected result. A solution of 10 parts of dipotassium salicylate, $\text{C}_6\text{H}_4\text{OKCOOK}$, and 34.5 parts of acetochlorhydrose in absolute alcohol was allowed to stand in the cold. After a short time a separation of potassium chloride began and continued for several hours. The solution was filtered, and deposited, on standing several days, clusters of needles. It is advisable to let the solution stand at least for ten days, as a separation of needles has been observed even after standing for that length of time. A better yield was obtained by allowing the filtrate from potassium chloride in a beaker to evaporate on the air. The needles were separated by filtration, washed well with alcohol, then with water, and crystallised several times from hot alcohol.

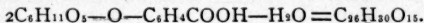
I. 0.2405 gram of substance, dried at 100° , gave 0.4720 gram CO_2 and 0.1208 gram H_2O .

II. 0.2725 gram of substance, dried at 100° , gave 0.5382 gram CO_2 and 0.1300 gram H_2O .

¹ Berichte der deutschen chemischen Gesellschaft, 8, 515.

			Found.	
Theory for $C_6H_{11}O_5-O-C_6H_4COOH$. $C_{26}H_{30}O_{15}$.			I.	II.
C	52.00	53.61	53.52	53.86
H	5.33	5.15	5.58	5.30

These results show conclusively that the glucoside of salicylic acid is not the direct product of the reaction. The substance formed stands in the relation of an ether or an anhydride to that compound :



It crystallises from alcohol in long, white needles, melting at $184-185^\circ$. They are insoluble in cold, sparingly in hot water; in cold alcohol slightly, they are easily soluble in warm alcohol. The aqueous or alcoholic solutions do not reduce Fehling's solution. Cold aqueous ammonia is without action; even if allowed to stand with it for several days the needles do not go into solution. When they are boiled for a long time with aqueous ammonia a gradual solution is effected. This solution reduced Fehling's solution, and also ammoniacal silver solution. A cold solution of caustic potash dissolves the substance very slowly in the cold; when heated it dissolves it easily. These solutions, heated to boiling, reduce Fehling's solution; and the addition of acids gave a precipitate of salicylic acid. In the filtrate the presence of dextrose was proved. The solution, made in the cold, does not reduce Fehling's solution, easily when heated with it. The substance is also decomposed into salicylic acid and dextrose by boiling with dilute acids. It is evident that the alkaline solution contained a glucoside of salicylic acid. The addition of acids to a very concentrated alkaline solution and extraction with ether gave a product consisting of salicylic acid and probably its glucoside, but several attempts to obtain the last substance in a pure state were fruitless.

The insolubility of the substance in aqueous ammonia proves that it does not contain carboxyl. This would seem to indicate that the substance is an anhydride of salicylic glucoside, a view which is corroborated by the investigation of its acetyl derivative. To prepare that compound the substance was heated in a water-bath with an excess of acetic anhydride and an equal weight of fused sodium acetate. The product of the reaction was boiled out with water, and the residue crystallised from alcohol. It forms long, white needles, which are insoluble in water, soluble in hot

alcohol. They melt at 110°–111°. It is insoluble in caustic potash; heated with it for some time it is decomposed into potassium acetate and salicylate, and dextrose. An analysis gave the following numbers:

0.2305 gram of substance, dried at 100°, gave 0.4658 gram of CO₂ and 0.1102 gram of H₂O.

	Theory for C ₂₆ O ₁₈ H ₂₂ (C ₂ H ₃ O) ₈ .	C ₂₆ O ₁₈ H ₂₂ (C ₂ H ₃ O) ₇ .	C ₂₆ O ₁₈ H ₂₂ (C ₂ H ₃ O) ₉ .	Found.
C	54.67	54.81	54.90	55.12
H	5.03	5.02	5.01	5.31

Although the carbon percentage obtained in the analysis agrees better with that of an octo-acetyl derivative than with those of derivatives containing a less number of acetyl groups, still the percentages of carbon in the various possible acetyl products approximate each other too closely that the results of the analysis should determine with any certainty the number of hydroxyls in the substance. An attempt to decompose the glucoside with $\frac{1}{10}$ standard sodium hydrate and titration gave no results, on account of the decomposition of the liberated dextrose by the alkali. More satisfactory results were obtained by decomposing the substance with dilute sulphuric acid and titration with alkali. The substance was heated in a closed tube with 10 cc. $\frac{1}{10}$ standard sulphuric acid for several hours at 120°, and the contents of the tube titrated with $\frac{1}{10}$ standard potassium hydrate. The liquid was colored slightly brown, which rendered the observation of the point of neutralisation difficult. There is, however, no greater uncertainty in the readings than 0.5 cc. of the alkaline solution.

I. 0.3615 gram of substance required 97.5 cc. $\frac{1}{20}$ standard KOH.

II. 0.5182 " " " 131.8 cc. " " "

	Theory for C ₂₆ O ₁₈ H ₂₂ (C ₂ H ₃ O) ₇ .	C ₂₆ O ₁₈ H ₂₂ (C ₂ H ₃ O) ₈ .	Found.	
CH ₃ CO	34.24	37.47	I. 36.7	II. 37.0

These results are strong evidence for the existence of eight hydroxyls in the compound. It is probably the anhydride of salicylic glucoside, and may be represented by

$\text{C}_6\text{H}_{11}\text{O}_5\text{—O—C}_6\text{H}_4\text{—CO—O—C}_6\text{H}_4\text{—CO—O—C}_6\text{H}_{11}\text{O}_5$. The formation of such a compound from acetochlorhydrose and dipotassium salicylate is difficult to understand; and, although the properties of the substance agree with those indicated by this constitutional formula, the question as to its constitution may still be considered open.

Synthesis of Methylarbutin.

Arbutin was supposed to be the glucoside of hydroquinone, having the formula $C_{12}H_{16}O_7$, until Hlasiwetz and Habermann¹ showed that when decomposed by acids a mixture of hydroquinone and methylhydroquinone in equivalent proportions was formed. These chemists changed the formula into $C_{12}H_{14}O_{14}$. Fittig,² somewhat later, called attention to the probability that natural arbutin is a mixture of the glucosides of hydro- and methylhydroquinone, and H. Schiff³ endeavored to separate the natural product by fractional crystallisation into these compounds. Pure methylhydroquinone glucoside was not obtained, but his results led him to conclude that the melting point of methylarbutin is in the neighborhood of 142° . In my first paper⁴ I had already called attention to the desirability of examining the action of acetochlorhydrose on the potassium derivatives of hydro- and methylhydroquinone, with the view of settling the constitution of natural arbutin. From methylhydroquinone⁵ a glucoside melting at 168° – 169° , and with about the same properties as arbutin, was obtained. Lately,⁶ Schiff has also obtained pure methylarbutin by the action of methyl iodide and potassium hydrate on arbutin, and found its melting point to be 175° – 176° .

An attempt to obtain hydroquinone glucoside synthetically gave no result. Hydroquinone dissolved in absolute alcohol gave a yellow solution on addition of sodium ethyl oxide. Acetochlorhydrose acted readily on this solution, forming acetic ether and sodium chloride, but from the filtrate a definite compound could not be obtained. Unsuccessful were also the experiments to isolate the monosodium derivative of hydroquinone. The yellow alcoholic solution gave on addition of ether a brown precipitate. This precipitate contained sodium, and gave hydroquinone when treated with acids; but it was only sparingly soluble in alcohol, and decomposed easily on exposure to the air, forming benzoquinone.

The experiments with methylhydroquinone gave more satisfactory results. This compound was prepared from arbutin (melting at 168° – 169°) according to the directions given by Hlasiwetz and Habermann. To prepare the potassium derivative⁷ pure potassium

¹ *Annalen der Chemie*, **177**, 342.² *Organische Chemie*, 10 Aufl. 638.³ *Annalen der Chemie*, **206**, 166.⁴ *This Journal*, **1**, 312.⁵ *Berichte der deutschen chemischen Gesellschaft*, **14**, 2100.⁶ *Ibid.* **15**, 1844.⁷ Körner and Bertoni, *Berichte der deutschen chemischen Gesellschaft*, **14**, 847.

hydrate was dissolved in absolute alcohol, the greater part of the alcohol evaporated and an equivalent of methylhydroquinone, also dissolved in a small quantity of absolute alcohol, added. This solution was mixed with 15–20 times its volume of anhydrous ether, which precipitated the potassium compound as a white crystalline powder. It was separated as much as possible by decantation, brought on a filter, washed with absolute alcohol, and dried *in vacuo* over sulphuric acid.

0.315 gram of potassium compound gave 0.1709 gram of K_2SO_4 .

K	Theory for $C_6H_4\overset{OK}{OCH_3}$.	Found.
	24.12	24.36

If the alcohol or ether used in the preparation of the potassium compound was not free of water, a part of the substance separated as an oil, which soon solidified to large, nacreous scales. This is probably an hydrate of the above compound. Both of the compounds are soluble in alcohol and water.

To an absolute alcoholic solution of the potassium derivative (1.1 parts), acetochlorhydrose (2.5 parts) was added, and the solution allowed to stand for several days. The clear solution soon deposited potassium chloride, and the odor of acetic ether was distinctly noticeable. It was then filtered, and the filtrate allowed to evaporate by exposure to the air. When a slight excess of the potassium compound was used the crystallisation began after the liquid had stood several days, otherwise not until a week, or often even longer. The crystals were well pressed between bibulous paper, dissolved in a small amount of hot water, filtered, and the filtrate placed over sulphuric acid in a closed vessel. The crystallisation took place very slowly, more rapidly if the sides of the vessel were occasionally rubbed with a glass rod. For analysis the substance was again crystallised from water.

I. .2548 gram of substance, dried at 120° , gave 0.5066 gram of CO_2 and 0.1532 gram of H_2O .

II. 0.2186 gram of substance, dried at 120° , gave 0.4354 gram of CO_2 and 0.1293 gram of H_2O .

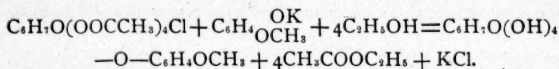
Theory for $C_6H_{11}O_5-O-C_6H_4OCH_3$.		Found.	
		I.	II.
C	54.54	54.23	54.32
H	6.29	6.67	6.57

The glucoside contains water of crystallisation; 0.347 gram of

substance, which had stood for several weeks on the air, lost 0.120 when heated to 120°.¹

Theory for 2(C ₁₃ H ₁₈ O ₇)H ₂ O.		Found.
H ₂ O	3.05	3.45

The substance has the empirical formula of methylarbutin. Its formation from acetochlorhydrose and potassium methylhydroquinone is represented as follows:



It crystallises from water in long, colorless, silky needles, which are concentrically grouped, and have a bitter taste. They melt at 168–169° and solidify again at 137–138°. Unlike arbutin, the solidified substance melted again at 168–169°. The substance is easily soluble in alcohol and water, insoluble in ether. The aqueous solution is not precipitated by basic lead acetate, nor by copper salts; it does not reduce Fehling's solution on heating. The aqueous solution is not colored blue by the addition of dilute aqueous iron trichloride. Digested with dilute mineral acids it is rapidly decomposed into dextrose and methylhydroquinone. This decomposition may also be effected by subjecting the aqueous solution to the action of emulsin. Concentrated nitric acid dissolves the glucoside to form a yellow solution, which, when boiled with alcohol and a small amount of sulphuric acid, then diluted with water, gave a violet color on addition of potassium hydrate. The aqueous solution heated with dilute sulphuric acid and manganese dioxide gave off the penetrating odor of benzoquinone.

A comparison of the properties of synthetical methylarbutin with those of arbutin shows that but in one respect a noticeable difference occurs. While an aqueous solution of arbutin is colored blue on addition of iron trichloride, that of the methyl compound remains unchanged. This property of arbutin is undoubtedly due to the presence of hydroxyl in the aromatic radical, and is therefore due to the presence of arbutin in the natural glucoside. In methylarbutin an hydroxyl in the aromatic radical does not exist, and its behavior towards the iron trichloride solution is in accordance with its constitution, since only those aromatic

¹ The percentage of water is somewhat high for the formula. It is possible that the substance loses part of its water of crystallisation by long standing on the air. When analysed no change in weight was noticed in 24 hours.

compounds containing that group show this property. It is evident from the similarity in the properties of arbutin and methylarbutin that a mechanical separation could only be effected with difficulty. H. Schiff,¹ who attempted the separation by repeated crystallisations from water, obtained a product melting at 142° , which he supposed to be nearly pure methylarbutin. Recently² he has shown that a mixture of two equivalents of arbutin and one of methylarbutin show the same melting point, and that methylarbutin itself melts at $175-176^{\circ}$.³ It may be safely inferred from the results of Schiff's and my own experiments that natural arbutin is a mixture of hydroquinone and methylhydroquinone glucosides in variable proportions.

Remarks on the Constitution of Salicin and Arbutin.

In my first paper⁴ attention was directed to the fact that the stability of helicin towards easily reducible metallic oxides is not in accordance with its constitutional formula, according to which it contains the formyl of dextrose. On the other hand, the synthesis of helicin from acetochlorhydrose and C_6H_4OKCHO , showed almost beyond a doubt that, whatever the constitution of dextrose might be, helicin is an ether of it and salicylaldehyde. Later,⁵ the suggestion was made that possibly in the oxidation of dextrose in alkaline solution by metallic oxides, the oxidation began at one of the carbinol groups of dextrose, and not as generally accepted at the formyl.⁶ If in place of the hydrogen

¹ *Annalen der Chemie*, **206**, 166.

² *Berichte der deutschen chemischen Gesellschaft*, **15**, 1842.

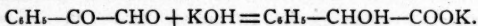
³ Schiff has called attention to the differences between the melting points and water of crystallisation in synthetical and natural methylarbutin. The melting point of salicin, one of the best examined glucosides, has lately been corrected from 198° to 204° : an imperceptible amount of impurity seems to lower considerably the melting points of the glucosides. In regard to the water of crystallisation, arbutin seems to have the property of crystallising with different amounts under slightly different conditions. Although I do not think there is the least doubt as to the identity of the two methylarbutins, I will prepare both products and carefully compare their properties.

⁴ *This Journal*, **1**, 304, 311.

⁵ *Berichte der deutschen chemischen Gesellschaft*, **14**, 2101.

⁶ H. Killiani sees in the stability of potassium gluconate and saccharate towards Fehling's solution a proof that the reduction is due to the presence of formyl. (*Berichte der deutschen chemischen Gesellschaft*, **14**, 2529.) Phthalic acid is readily oxidised by potassium permanganate, whereas sodium phthalate in presence of an alkali is very stable towards that oxidising agent. (Weith, *Berichte der deutschen chemischen Gesellschaft*, **7**, 1058.) This shows that the effect of replacing the hydrogen of the carboxyl is to strengthen the affinity of the carboxyl to the carbon atom it is united with. It is evident that no conclusion can be strictly drawn from a difference in the behavior of the alkaline salt of gluconic acid and an alkaline solution of dextrose. Hlasiwetz and Habermann used gluconic acid, and this may be the reason of the difference between their observations and those of Killiani.

of the hydroxyl where the oxidation begins, a stable radical is substituted, a greater stability of the new product seems probable. Some observations have recently become known that make the existence of a formyl group in dextrose doubtful. Breuer and Zincke¹ have shown that benzoyl and acetylcarbinol in alkaline solution reduce copper oxide, forming phenylhydroxyacetic and lactic acids. They concluded, in their first paper, from these facts that the reducing property of dextrose may be owing to the presence of $\text{CO}-\text{CH}_2\text{OH}$. These chemists attempted to explain the above facts by assuming the decomposition of the compounds in benzoic, acetic and formic aldehydes, and then by the reuniting of benzoic and acetic aldehydes with formic aldehyde the formation of the aldehydes of phenylhydroxyacetic and lactic acids. V. Meyer² considers the conversion of the carbonyl-carbinols into hydroxy-acids as perfectly analogous with the oxidation of dextrose into gluconic acid, and explains the reaction by assuming that it is due to action of water and the oxygen of the oxide: $\text{R}-\text{CO}-\text{CH}_2\text{OH} + \text{H}_2\text{O} + \text{O} = \text{R}-\text{CHOH}-\text{COOH} + \text{H}_2\text{O}$. I have explained this reaction³ in a somewhat different manner. According to it the copper oxide converts the carbinol group into formyl, and then the alkali acts, as on all aromatic aldehydes, oxidising and reducing:



V. Meyer in comparing the formation of gluconic acid from dextrose with that of phenylhydroxyacetic acid from benzoylcarbinol overlooked a very important fact, to which attention was called in my note. Under the same conditions that dextrose goes over into saccharic acid, oxidation in acid solution (nitric acid), benzoylcarbinol does not give the hydroxy-acid, but benzoic and benzoyl formic acids. Breuer and Zincke's results might be accepted as a proof of the presence of carbonyl in dextrose, if an acid containing it were obtained by oxidation with nitric acid; as the facts now stand their experiments may be given as a proof that dextrose does not contain that radical. Zincke's view as to a previous decomposition into benzoic and formic aldehydes is difficult to understand. Formic aldehyde is extremely easily decomposed by alkalies, besides being equally easily oxidisable by metallic oxides. A second hypothesis, which he considers pos-

¹ Berichte der deutschen chemischen Gesellschaft, **13**, 635; Annalen der Chemie, **216**, 311.

² Berichte der deutschen chemischen Gesellschaft, **13**, 2344.

³ Ibid. **14**, 2100.

was much better in accordance with the properties of helicin than that assuming the existence of the formyl of dextrose. Attention was also directed to the fact that such a compound could on decomposition by acids give dextrose, considered as containing formyl. In view of the observations of Schmidt regarding dextrose, it seems to me that the above, or a similar formula differing only in regard to which of the secondary carbinol groups take part in the condensation, best represents our present knowledge of the constitution of helicin. The same may be said to apply to the constitutional formulae of salicin, methylarbutin and probably most of the glucosides. In regard to salicin the following experiment is strongly confirmatory of the non-existence of formyl in it. Salicin was dissolved in alcohol and treated for several days with sodium amalgam. Care was taken to prevent the solution becoming very alkaline by addition of acetic acid. It was found that the salicin remained unchanged, whereas under these conditions dextrose is converted into mannite.

TUFTS COLLEGE, May 12th, 1883.

ON THE FORMATION OF CROTONIC AND β -OXYBUTYRIC ALDEHYDES FROM ETHYL ALDEHYDE.¹

BY ARTHUR MICHAEL AND ADOLPH KOPP.

Among the many important contributions which have been made of late years to organic chemistry, few have attracted and merited more attention from chemists than synthesis by dehydration. The interest felt in this class of reactions is in no small measure due to the belief that they play a prominent role in some of the most important of all syntheses occurring in vegetable nature, the formation of carbohydrates from carbonic acid and water. The suggestion that dextrose may be formed by the dehydration of an hypothetical hydrate of formic aldehyde, and that from it the vari-

¹ The experiments described below were made in December, 1878, in the chemical laboratory of the École de Médecine in Paris. A preliminary notice is found in the Bulletin de la Société chimique (1879) **31**, 434, and also in the Berichte der deutschen chemischen Gesellschaft, **12**, 2091. The research has not attained the completeness which we had hoped to give it; but, as it is improbable that we shall together ever be able to resume work on it, we consider it advisable to publish it in its unfinished state.

ous other carbohydrates are formed, was first made by Baeyer; while Kekulé, deducing from the interesting results of his investigation on the condensation products of ethyl aldehyde, also called attention to the probability of similar reactions occurring in nature. However, not only in these views, but in the whole theory of synthesis by dehydration, there was such an element of uncertainty and improbability that the famous research of A. Wurtz on the formation of aldol from ethyl aldehyde may be considered as the beginning of a new epoch in this department of chemistry. The distinguished French chemist concluded, in view of the formation of aldol by the action of chlorhydric acid on ethyl aldehyde in the cold, it was probable that the formation of crotonic aldehyde by chlorhydric acid in the heat was preceded by that of β -oxybutyric aldehyde. Crotonic aldehyde has been obtained, not only by the action of chlorhydric acid, but by zinc chloride and several other salts, whereas the formation of aldol has not been observed in their action on ethyl aldehyde. Moreover, in Wurtz's experiments a considerable quantity of acid was used; while it has been found that a small quantity of acid or zinc chloride was able to form a large amount of crotonic aldehyde. If Wurtz's view as to the previous formation of β -oxybutyric aldehyde is capable of generalisation, in all cases when the formation of crotonic aldehyde has been observed, only proper conditions, the previous formation of β -oxybutyric aldehyde should be provable. The following experiments were made with this object, and also to ascertain whether salts which occur in vegetable nature have the property of carbon-polymerising¹ ethyl aldehyde.

Before describing these experiments, we shall give a brief review of what had been done on the subject up to the time when we published a preliminary notice, which gave the principal results of the investigation. The formation of crotonic aldehyde from ethyl aldehyde was first noticed by Wurtz and Bauer² and Lieben,³ the former chemists obtaining it by the action of zinc chloride on ethylene alcohol and aldehyde, the latter by the action of concentrated solutions of potassium formate, sodium acetate, and sodium potassium tartrate at 100° on ethyl aldehyde. This chemist gave crotonic

¹ Carbon-polymerisation is used in this paper when the polymeride is formed by linking of carbon to carbon; oxygen-polymerisation when it is due to the linking of oxygen atoms. β -Oxybutyric aldehyde is an example of the first, paraldehyde of the second class.

² Comptes rendus, 51, 55.

³ Annalen der Chemie, Suppl. 1, 114.

aldehyde its correct empirical formula. Our knowledge of the constitution of crotonic aldehyde is principally due to the important investigation of Kekulé,¹ who, by oxidising it to solid crotonic acid, proved it to be the aldehyde of that acid. This experiment characterised it as a butyl derivative, a view previously suggested by Baeyer.² The action of sodium and zinc on ethyl aldehyde has been studied by J. Riban,³ who obtained β -oxybutyric aldehyde and the compound $C_6H_{10}O_2$ as products of the reaction. The behavior of isoamylaldehyde towards heat, sodium, and caustic potash had been previously studied by A. Borodin.⁴ He obtained by the action of heat and sodium condensation-products of the aldehyde; by the action of the alkali, polymeric products that decomposed on distillation into the original aldehyde. The action of potassium carbonate in the cold gave Borodin's polymeride, while in the heat condensation-products are formed.⁵ A somewhat different observation was made by Bruylant,⁶ who obtained in the same reaction a solid polymeric aldehyde, while the above chemists obtained liquid products. This compound likewise decomposed into isoamylaldehyde on heating. Simultaneously with our investigation, F. Urech⁷ examined the action of potassium carbonate on isobutyl aldehyde. In the cold a polymeride was formed that decomposed on heating, partially into isobutylaldehyde, in part into condensation-products of that compound. In the heat only the latter products were formed.

Action of Zinc Chloride on Ethyl Aldehyde.

The experiments of Kekulé on the action of zinc chloride on ethyl aldehyde are of special interest. He observed that a very small amount of zinc chloride sufficed to cause the formation of a considerable quantity of crotonic aldehyde, and that this even took place in presence of water. Kekulé's method for the preparation of crotonic aldehyde is to heat the mixture at 100° , and then distill. These are conditions under which β -oxybutyric aldehyde decomposes into crotonic aldehyde and water. In the following experiments the products of the reaction were separated under conditions permitting the isolation of the oxyaldehyde.

¹ *Annalen der Chemie*, **162**, 77.

² *Annalen der Chemie*, Suppl. **5**, 81.

³ *Bulletin de la Société chimique*, **18**, 63.

⁴ *Berichte der deutschen chemischen Gesellschaft*, **2**, 552; **3**, 423; **5**, 481; **6**, 982.

⁵ *Gäss and Hell, Berichte*, **8**, 369.

⁶ *Ibid.* **8**, 415.

⁷ *Ibid.* **12**, 191, 1745.

I. A sealed tube containing pure ethyl aldehyde, several drops of water, and a very small quantity of zinc chloride was heated for 24 hours at 90° . The contents of the tube, which had the penetrating odor of crotonic aldehyde, was brought into a boiling-flask and distilled under a pressure of 25 mm. The fraction passing over between 80° – 120° dissolved almost entirely in water. The solution was filtered, and evaporated *in vacuo* over sulphuric acid. A thick liquid was obtained, which showed all the properties of β -oxybutyric aldehyde, and decomposed on distillation into crotonic aldehyde and water.

II. It seemed probable that in the above experiment, owing to the continued action of heat, a part of the oxyaldehyde had decomposed into crotonic aldehyde. A second tube, prepared like the first, was heated for twelve hours. The contents of this tube had but a faint odor of crotonic aldehyde. It was distilled *in vacuo*, the fraction between 80° – 130° again distilled, and that portion passing over between 90° – 110° dissolved in water, filtered, and the solution evaporated *in vacuo*. On analysis the following numbers were obtained :

0.6283 gram of liquid gave 1.2435 gram of CO_2 and 0.5629 gram of H_2O .

Theory for $\text{CH}_3\text{—CHOH—CH}_2\text{—CHO}$.		Found.
C	54.54	53.97
H	9.09	8.96

The liquid was β -oxybutyric aldehyde. On long standing it thickened, and finally solidified to the para-compound.

III. The formation of oxybutyric aldehyde takes place in the cold, though very slowly. A tube, prepared as the above, was allowed to stand for ten days at 20° , and was then found to contain a small quantity of aldol.

IV. Par-aldehyde, in aqueous solution, is not converted in the cold into aldol. After the mixture was heated for ten hours at 100° the formation of aldol was proved. It is probable that the formation of aldol is due to the decomposition of par-aldehyde into aldehyde by the action of heat.

These experiments show conclusively that the first product of the action of zinc chloride on ethyl aldehyde is β -oxybutyric aldehyde and not crotonic aldehyde.¹ With this proof Kekulé's

¹We made several experiments on the action of zinc chloride on a mixture of chloral and ethyl aldehyde. The mixture allowed to stand for some hours at about 30° became very thick.

elaborate hypothesis on the function of zinc chloride in this reaction becomes superfluous. In fact, the assumption of the existence of anhydrous molecules of zinc chloride in its aqueous solution, and their preferring to dehydrate ethyl aldehyde in order to get water, instead of uniting with water already formed, was sufficient to make his views extremely improbable at the time of their publication. It is possible, as Kekulé has suggested, that the action of zinc chloride may be due to the presence of free chlorhydric acid in its aqueous solution; but, whether it be due to presence of free acid or to zinc chloride, our knowledge of the functions of these substances in the aldol formation may be said to be limited to bare facts.¹

Action of Potassium Salts on Ethyl Aldehyde.

Lieben, in his research on the action of weak affinities on ethyl aldehyde, examined the action of concentrated solutions of potassium formate and sodium acetate, and obtained crotonic aldehyde. We repeated his experiments, with a view of proving the previous formation of aldol. A solution of ethyl aldehyde in concentrated aqueous potassium formate heated in a sealed tube at 100° gradually divided into two layers, the upper consisting of a thick yellow oil, which increased in viscosity with continued heating. This oil has, according to Lieben, the composition of crotonic aldehyde, and yields it on distillation. It certainly contained that substance mixed with higher condensation products, and, probably, compounds that decompose into crotonic aldehyde on distillation. If

On distillation *in vacuo* a heavy oily liquid passed over between 120°–125°, which was insoluble in water. When heated under ordinary pressure it gave off chloral and aldehyde, even when distilled *in vacuo* a slight decomposition into these products was noticed. The analyses of different preparations showed that a definite product cannot be obtained by distillation (Cl = 47.73; 38.76; 42.88; C = 27.97; H = 3.45). The compound is probably an oxygen-polymeride of chloral and ethyl aldehyde. If the mixture of chloral and aldehyde is heated at 100° a violent reaction ensues, resulting in a complete decomposition of the substance used.

¹Experiments which have recently been made in the chemical laboratory of Tufts College put the function of acids in an analogous reaction, the action of aromatic aldehydes on phenols, in an entirely new light. Baeyer in most of his experiments used a considerable quantity of concentrated acids, ostensibly for the purpose of dehydration. There is no connection between the affinity of the acids for water and the reaction. To take a special case, a mixture of one part of resorcin and one part of benzoic aldehyde dissolved in two parts alcohol, is converted by the merest trace of chlorhydric acid—the temperature of the mixture rises to about 60°—quantitatively into an amorphous compound, $C_{26}H_{20}O_4$. The further action of acids, no matter how dilute, on this resin, is to convert it into a mixture of two crystalline compounds, one of which is isomeric with it. This compound has all the properties of a crystallisable resin, and undoubtedly belongs to that group. A full account of the investigation will appear in an early number of this Journal.

A. MICHAEL.

aldol were formed it should be found in the aqueous layer. This was extracted with ether and the extract distilled *in vacuo*. Between 90–110° an oil passed over, but it was only slightly soluble in water, and certainly did not contain more than a trace of aldol.

These results led us to examine the behavior of aldol towards potassium formate, under like conditions. This compound was completely decomposed into the same products obtained from ethyl aldehyde. It is evident that the conditions of the experiment precluded the existence of aldol, even if it had been formed in the reaction. In the second experiment a dilute solution of potassium formate was used. Two grams of the salt were dissolved in 40 grams of distilled water, and the solution mixed with an equal volume of ethyl aldehyde. This mixture was heated in a sealed tube for six hours at 100°, and gave after heating a homogeneous liquid, smelling slightly of crotonic aldehyde. The undecomposed ethyl aldehyde was expelled by gentle heating, the liquid extracted with ether, and the residue remaining after evaporation of the ether distilled *in vacuo*. Between 90–110° a considerable quantity of a liquid passed over, which an examination showed to be aldol. Several experiments were made in order to ascertain the minimum concentration of aqueous potassium formate which would form aldol. A solution of 1 gram of salt in 40 grams of water and an equal volume of aldehyde gave, after heating 48 hours, a considerable amount of aldol; while a solution containing but 0.5 gram of salt and the other compounds as above, did not yield aldol, even after heating several days.

It may be inferred with considerable certainty that the formation of crotonic aldehyde by the action of potassium formate is preceded by the formation of β -oxybutyric aldehyde. The property of carbon-polymerising ethyl aldehyde to aldol is not confined to potassium formate. It was shown by every potassium salt we examined whose aqueous solution possesses an alkaline reaction, and it only needs the confirmation of experiment to give certainty to the generalisation that all such potassium compounds have this property. A solution of 15 parts of dipotassium phosphate in 30 parts of water, and ethyl aldehyde added until the salt began to separate, contained aldol after heating. A small quantity of an oil, containing crotonic aldehyde, separated from the liquid, probably due to the action of the salt on aldol.

A tube with potassium acetate, prepared like the above, also gave aldol. In this experiment a much larger amount of oil had separated from the solution.

The same result was obtained by using an aqueous solution of potassium carbonate. Very interesting is the action of the dry salt on aldehyde. Bruylants,¹ who had already made this experiment, found that the aldehyde was completely converted into resinous products. The action is indeed very violent, and nothing but resinous products are obtained, unless care be taken to cool the aldehyde and carbonate before bringing them together. With this precaution, however, the reaction proceeds slowly, and after several hours the mixture may be allowed to stand at the ordinary temperature. After standing two days the liquid had assumed the consistency of aldol, and the carbonate was dissolved in the liquid. The slightly yellow liquid was dissolved in water, the solution extracted with ether, and the extract treated in the usual way for the preparation of aldol. The yield of this substance was so considerable that we can recommend the method for its preparation.

The neutral potassium salts examined in respect to their behavior towards ethyl aldehyde, were the sulphate, nitrate and chloride. Mixtures of two parts of aldehyde and one of water were saturated with these salts, and heated in closed tubes at 100°. In no case, even after prolonged heating, was a change noticed in the contents of the tubes.

The action of potassium salts whose aqueous solutions show an alkaline reaction may be owing to the presence of a small amount of free alkali in the solution, as it is not improbable that the alkaline reaction is due to a slight decomposition of such salts into free alkali and an acid salt. Lieben had already made an experiment on the action of potassium hydrate on aldehyde, in the hope of obtaining crotonic aldehyde. A heavy red liquid, insoluble in water, was obtained, which was considered as an intermediary product between crotonic aldehyde and aldehyde-resin. We can confirm this result, but the oil is only formed by long heating from the first product of the reaction. If a very dilute solution of caustic potash is mixed with an equal volume of aldehyde, and the mixture heated for two hours at 90°, but little of this oil separated from the liquid. Extracted with ether and examined for

¹ *Berichte der deutschen chemischen Gesellschaft*, **8**, 415.

aldol, the presence of this compound was shown. Aldol, when heated with dilute aqueous caustic potash, is gradually converted into the heavy oil. There is, however, no proof that the salts themselves do not possess the property of forming aldol; indeed, in one instance, its formation by the action of dry potassium carbonate on anhydrous aldehyde, this has been shown to be the case.

Action of Sodium Salts on Ethyl Aldehyde.

Lieben in his experiments on the action of sodium acetate used a concentrated solution of that salt, and obtained crotonic aldehyde. The experiment was repeated, with the difference that the tube was heated only to 80° for ten hours. After heating the liquid was separated into two layers. The supernatant liquid, distilled *in vacuo*, gave crotonic aldehyde, and an oily, higher boiling liquid, which was insoluble in water. This oil may have been formed by the action of the salt on crotonic aldehyde, since it was found that the same, or a very similar product, can be obtained by heating crotonic aldehyde with aqueous sodium acetate. The lower layer was extracted with ether, the ether evaporated, and the oily residue extracted with a small amount of water. The greater part of the oil did not dissolve in it; on distillation *in vacuo*, crotonic aldehyde was obtained. The soluble portion, on evaporation *in vacuo*, left an extremely small amount of a thick liquid, which but partly dissolved on second treatment with water. It is possible that this liquid contained a minimum amount of aldol, but the quantity of the liquid obtained was too small to permit its isolation. The reaction was then examined, using dilute solutions of sodium acetate. Under these conditions a somewhat greater quantity of the soluble thick liquid was obtained, but not enough to purify it by distillation. We believe that a small amount of aldol is formed in the reaction; it was very evident, however, that in all of our experiments crotonic aldehyde, and compounds decomposing into it on distillation, are the main products of the reaction.

Potassium formate acts readily on aldehyde, forming aldol; in striking contrast appears the following experiment with sodium formate. A mixture of equal volumes of aldehyde and a saturated solution of sodium formate was heated for several days at 100° . The salt is but slightly soluble in concentrated aqueous aldehyde. On heating at 100° more dissolved and crystallised out from the

solution on cooling. The aldehyde was found to remain unchanged.¹ A tube with disodium phosphate was prepared by mixing equal volumes of a saturated aqueous solution of the salt and ethyl aldehyde, and then adding sufficient water to dissolve the salt which had separated. After heating at 100° the supernatant oil of the liquid was found to distill between 80° and 210°, and yielded mainly crotonic aldehyde. The aqueous solution gave the same results as the experiment with sodium acetate.

Very noteworthy is the difference between the behavior of sodium and potassium carbonates. Dry sodium carbonate is, at ordinary temperature, without action on anhydrous aldehyde; even if allowed to stand in contact with it for several months.

Like the neutral potassium salts, solutions of the corresponding sodium salts were found to be without action on ethyl aldehyde.

Finally a very dilute solution of sodium hydrate was heated with aldehyde. The results were about the same as those obtained with potassium hydrate. A sufficient quantity of aldol was obtained to prove its formation beyond a doubt, but the amount formed under the same conditions was much less than with the potassium compound.

The following are the principal results of the investigation:

1. The primary product of the action of zinc chloride on ethyl aldehyde is β -oxybutyric aldehyde.
2. Neutral sodium and potassium salts have no action on ethyl aldehyde.
3. Alkaline potassium salts, sodium and potassium hydrates act like zinc chloride. The presence of water is not always necessary, as dry potassium carbonate acts in the same manner.
4. Alkaline sodium salts, under the same conditions as potassium salts, form principally crotonic aldehyde, oily substances, and probably a small amount of β -oxybutyric aldehyde. Dry sodium carbonate has no action on aldehyde.
5. β -oxybutyric aldehyde heated with moderately concentrated solutions of alkaline salts or zinc chloride, is converted partly in crotonic aldehyde, and partly in higher boiling oils, that decompose into crotonic aldehyde on distillation. Crotonic aldehyde itself undergoes a change to higher boiling products.

¹ Experiments with dilute solutions of this salt were also made. Unfortunately the results were not written down in our notebook. We believe that a small amount of oily products, giving crotonic aldehyde on distillation, were obtained, but no aldol, at least not in appreciable quantity.

It would be premature to discuss whether, in the action of alkaline sodium salts, the formation of crotonic aldehyde is preceded by that of β -oxybutyric aldehyde. The experiments with sodium and potassium formates, carbonates and phosphates show, beyond a doubt, that potassium salts possess in a much greater degree than sodium salts the property of carbon-polymerising ethyl aldehyde. This is a clue to the function of potassium salts in the vegetable world that should not be lost sight of. The retention of potassium salts by the soil, their absorption by plants as essential constituents for life, and the property of these salts of converting aldehydes into oxyaldehydes of higher series, are evidently intimately related; especially as recent researches have made it probable that the first product in the formation of the carbohydrates is the aldehyde of the methyl group.¹

COLLEGE HILL, MASS., June 20th, 1883.

¹ We made a large number of experiments on the action of potassium salts on methyl aldehyde (see Bulletin de la Société chimique (1879), **31**, 434; this Journal, **1**, 418). The salts used were potassium carbonate, formate and phosphate. The proportion was about one part of salt to ten parts of aldehyde in aqueous solution, and the experiments were made in closed tubes heated at 100°. The product of the reaction contains a dark colored syrup, which was purified by partial precipitation with basic lead acetate, filtration from the dark precipitate, and repeating until a white precipitate was obtained, which was suspended in water and treated with hydrogen sulphide. The filtrate was evaporated to dryness and the residue extracted with absolute methyl alcohol, filtered and again evaporated. The syrup, which had a slightly bitter taste, reduced Fehling's solution, apparently however not so strongly as dextrose does. It gradually hardened, but no sign of crystallisation was observed, even on standing several months. Heated with acetic anhydride and sodium acetate, a syrup, insoluble in water, was formed, but a crystalline product was not formed, as might be expected if the syrup contained dextrose. The analysis of the lead compound showed that the constitution of the syrup differed somewhat according to the conditions of its preparation. The results were, 67.3, 67.6, 68.1, 67.9 per cent. of PbO. According to Pelletier and Stein, the corresponding lead derivative of dextrose contains 66.27 per cent. of PbO. The proximate analysis of the syrup, dried at 100°, gave the following numbers:

		Found	Theory for	
			C ₆ H ₁₀ O ₆	C ₆ H ₁₂ O ₆
C	42.9	43.4	43.7	44.4
H	6.3	6.2	6.6	6.17
				49.0
				6.6

The analyses were made with products of different preparations. It is probable that the syrup obtained by the action of alkaline potassium salts is the same as that obtained by Butlerow by the action of alkalis or barium hydrate; a reaction which has lately been re-examined by Tollens (Berichte der deutschen chemischen Gesellschaft, **16**, 919).

LABORATORY NOTES.—II.¹

BY ARTHUR MICHAEL.

V.—ON THE ACTION OF SODIUM ETHYL OXIDE ON BROM-ETHYLIDENEBROMIDE.

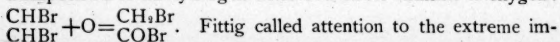
According to Tawildarow² sodium ethyl oxide acts on bromethylidenebromide, forming a mixture of two dibromethylenes; the bromide boiling at 91°, and a second compound boiling at 157°. A third isomeride, boiling at 109°, has been obtained by Sabenejeff;³ either by direct addition of bromine to acetylene, or by reduction of acetylene tetrabromide. The existence of three dibromethylenes is of great theoretical importance, since it necessitates the assumption of a so-called dyad carbon atom in one of the compounds. The bromethylidenebromide used by Tawildarow was isolated from the products of the action of bromine on ethylbromide; and, as the perfect separation of the products of that reaction is somewhat difficult, it was thought of sufficient interest to repeat his experiment, using a pure product obtained by the addition of bromine to bromethylene. It may be mentioned that Tawildarow supposed the product boiling at 157° to be identical with acetylene dibromide, and that the later investigation of Sabenejeff, and also that of Anschuetz,⁴ show that this is not the case.

The experiment was repeated under exactly the conditions stated by Tawildarow. The formation of bromacetylene was noticed. The greater part of the product of the reaction passed over under 95°, and gave on redistillation *a*-dibromethylene, boiling at 86–88°. Above 95° the thermometer rose rapidly to 180–190°, at which temperature undecomposed bromethylidenebromide passed over. The products of the reaction of equal molecules of sodium ethyl oxide and bromethylidenebromide (from bromethylene) are, therefore, bromacetylene, *a*-dibromethylene and unchanged bromethylidenebromide. The results of the analyses and vapor density given by Tawildarow for the dibromethylene boiling at 157°, agree fairly with the numbers required by theory; but

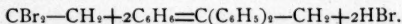
¹ This Journal, **1**, 473.² *Annalen der Chemie*, **176**, 22.³ *Ibid.* **178**, 116; *Berichte der deutschen chemischen Gesellschaft*, **9**, 1441.⁴ *Berichte der deutschen chemischen Gesellschaft*, **12**, 2073.

before so important a fact as the existence of a third dibromethylene can be accepted, more decisive proof of the homogeneity and nature of the product is necessary; especially in view of the result obtained from the pure bromethylenebromide used in the above-described experiment.

It may not be unprofitable to review the recent discussions on the constitution of the dibromethylene boiling at 88° . Demole, in his first paper, when he showed that this compound absorbs free oxygen passing over into bromacetylbromide, assumed that the dibrom compound was identical with acetylene dibromide, and attempted to explain the formation of bromacetylbromide by a transposition of an hydrogen atom and direct addition of oxygen:



Fittig called attention to the extreme improbability of such a reaction, and proposed, as best explaining its properties, the formula $\text{CH}_2\text{Br}-\text{CBr}$. The next contribution was made by Anschuetz,¹ who, by confirming Sabenejeff's experiments on acetylene dibromide, showed that chemist's compound is identical with the dibromide in question. Demole² had, in the meantime, arrived at the same conclusion in a different manner. He examined the action of aluminium chloride on a mixture of dibromethylene (88°) and benzene, and obtained unsymmetrical diphenylethylene. Although Demole accepted Fittig's formula as the simplest explanation of the behavior of dibromethylene towards oxygen, he considered the formation of unsymmetrical diphenylethylene as a conclusive proof of an unsymmetrical distribution of the bromine in α -dibromethylene. A compound of the formula $\text{CH}_2\text{Br}-\text{CBr}$ should have given $\text{C}_6\text{H}_5-\text{CH}_2-\text{C}-\text{C}_6\text{H}_5$; the reaction which took place is represented, according to Demole, as follows:

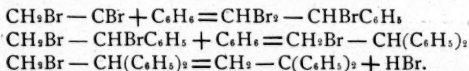


This experiment seems to have been very generally accepted as proving the constitution of α -dibromethylene. In reality the experiment gives no decisive proof in regard to the constitution of that compound, as it depends entirely on the interpretation which has been given to the reaction. It is a well-known property of the halogen derivatives of unsaturated hydrocarbons that the halogen atoms are either not replaceable, or only with difficulty, by

¹ Berichte der deutschen chemischen Gesellschaft, 12, 2073.

² Ibid. 12, 2245.

other groups. In this respect there is but little difference between the aromatic and paraffin compounds; the halogen derivatives of benzene act like the halogen derivatives of an alkylene, or, more strictly, an alkylacetylene, in which the halogen is connected with an unsaturated carbon atom. The proof that these unsaturated halogen hydrocarbons act in the Friedel reaction like the saturated compounds is still to be given. It is improbable, in view of the difficulty with which this class of compounds enter into double decompositions. The reaction examined by Demole is susceptible of quite a different interpretation. Shortly before, Balsohn¹ had shown that ethylene passed into the benzene-aluminium chloride mixture is absorbed with the formation of ethylbenzene. Here we have a reaction which is analogous to Demole's. If ethylene unites to form ethylbenzene, dibromethylene will unite, probably with much greater ease, to form dibromethylbenzene. In this saturated compound the conditions are given for the replacement of bromine by phenyl by means of Friedel's reaction. From $\text{CBr}_2\text{—CH}_2$ the compounds $\text{CBr}_2\text{C}_6\text{H}_5\text{—CH}_3$ or $\text{CBr}_2\text{H—CH}_2\text{C}_6\text{H}_5$, from $\text{CH}_2\text{Br—CBr}$, the compound $\text{CH}_2\text{Br—CBrHC}_6\text{H}_5$ may be formed; and it is evident that from the first and third of these compounds, by replacing a bromine by phenyl and splitting off of bromhydric acid, unsymmetrical diphenylethylene may be obtained:



Demole² published in the following year a new series of experiments on the action of oxygen on α -dibromethylene. In this paper the previous explanation is given up, because an experiment showed that oxygen and bromhydric acid passed into bromacetylene do not yield bromacetyl bromide. He now considered the reaction as due to the displacement of bromine by oxygen, and addition of bromine to the hypothetical compound thus formed. Demole's method of proof is here exactly as decisive as in his previous papers. Certain well-known reactions are given a dogmatic interpretation, and it is applied to the reaction in question. When bromine separates from a concentrated solution of bromhydric acid exposed to the action of oxygen, it is, according to

¹ Bulletin de la Société chimique, **31**, 540.

² *Ibid.* **34**, 201.

Demole, due to the displacement of bromine by oxygen. How will he prove that it is not due to the oxidation of bromhydric acid to hypobromous acid, which, as is well known, is decomposed by bromhydric acid into bromine and water? Again, a large number of bromides when exposed to the air attract water, and are converted into acids. When phosphorus tribromide is converted by water into phosphorous acid, according to Demole, the water is first decomposed into hydrogen and oxygen, the latter element then displaces the bromine, which unites with the hydrogen, and finally the acid anhydride takes up water to form phosphorous acid. The usual interpretation is, of course, a simple double decomposition between the water of the air and the tribromide. As further proof, an exceedingly interesting experiment on the action of oxygen on boiling phosphorus tribromide is given. The products formed are phosphorus pentabromide and oxybromide. The conclusion drawn from the experiment is, that oxygen displaces bromine to form POBr , which unites with bromine to form POBr_2 , and with PBr_3 to give PBr_5 . Unexplained is how two atoms of bromine do the work of four; or else the liquid contained POBr , a point still to be proven. It is at present impossible to give any decisive proof regarding the formation of the pentabromide. Homogeneous phosphorus trichloride is perhaps entirely unknown. As Casselmann¹ has shown the distilled compound deposits phosphorus, it consists, not unlikely, of a large proportion of trichloride with phosphorus and pentachloride. A decisive proof that the formation of oxychloride by the action of oxygen on trichloride is due to the direct addition of oxygen to the trichloride has yet to be given. Or, it is possible that, under the above conditions, POBr_2 may act on PBr_3 , forming oxide and pentabromide. Finally, dried air was passed for ten hours through α -dibromethylene. The gases passed out through a series of well-cooled tubes, and then into a flask containing bromine. This flask was found to contain tetrabromethene, and the first vessel bromoacetyl bromide, bromoacetic acid and a polymeride of $\text{C}_3\text{H}_2\text{Br}_2$. The explanation: oxygen breaks, in a peculiar manner (*façon speciale*), the "double carbon-link" forming the compound $-\text{CBr}_2-\text{CH}_2-$. This product is extremely volatile—so much that it passed through a tube surrounded by a mixture of ice and salt, and was absorbed in the bromine flask, forming $\text{CBr}_2-\text{CH}_2\text{Br}$. The com-

¹ Annalen der Chemie, **83**, 267.

pound also undergoes, especially at a high temperature, a decomposition represented as follows: $-\text{CH}_2-\text{CBr}_2-\text{O}=\text{CH}_2$, $-\text{C}=\text{O}+\text{Br}_2$; $-\text{CH}_2-\text{CO}-\text{O}=\text{CH}_2$, $-\text{COBr}$. The climax of the double and triple linkage theory has here been reached. This theory supposes that there are no less than three different kinds of linkage; or, rather, carbon may be linked to carbon in three different ways. In the first kind the carbon atoms, as in saturated hydrocarbons, are not "ruptured" by the action of halogens; the second variety of linkage is shown in unsaturated hydrocarbons, where a "rupture" occurs until the compound becomes saturated; and, finally, the existence of a third variety is supposed, where, even in saturated compounds, a "rupture" takes place, but on reduction with nascent hydrogen it is healed. And now Demole supposes that a characteristic property of compounds with ruptured carbon-linkage is extreme volatility.

It may be well, before proceeding further in this maze of hypotheses regarding double and triple linkage, to inquire for its credentials. How do we know that double or triple linkage occurs in unsaturated organic compounds? What facts necessitate this hypothesis? But two plausible reasons have been brought forward. The attempts that have been made to obtain methylene and ethylidene have not succeeded, in each case ethylene gas was obtained; and that methyl is not known in a free state. The experiments with methyleneiodide prove nothing in regard to a possible existence of methylene. The first product in the action of copper, reasoning from analogy with methyl iodide, is ethyleneiodide, which, as is well known, on heating with metals goes over into ethylene. The same applies to the action of sodium at a high temperature on ethylidenechloride. There is no necessity for supposing the previous formation of ethylidene; the chloride heated to a high temperature gives off chlorhydric acid,¹ and this will naturally occur much more readily in the presence of a substance like sodium, which has a strong affinity for the acid. Given chlorhydric acid, sodium and chlorethylene, and we have all the conditions requisite for the formation of ethylene. Equally cogent is the non-existence of methyl. All that can be said on the subject is, that it is a property of this radical, under the conditions of the experiments, to pass over into a saturated hydrocarbon. But if compounds like methylene and ethylidene are

¹ Kraemer, *Berichte der deutschen chemischen Gesellschaft*, **12**, 204.

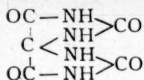
not known, it is only necessary that part or all of the hydrogen of these hydrocarbons should be replaced by negative elements or groups to give stable compounds. The existence of CO, of $\text{CH}_3-\text{N}-\text{C}$, of $\text{HOOC}-\text{CH}_2-\text{C}-\text{COOH}$, and probably of $\text{CH}_2\text{Br}-\text{CBr}$, shows this beyond a doubt. A general property of this class of substances is the marked affinity of the unsaturated carbon for oxygen. CH_3NC and HgO give CH_3NCO ; and Demole has shown the still more pronounced affinity of $\text{CH}_2\text{Br}-\text{CBr}$. I have used Demole's researches as an example of the deteriorating influence which the double and triple linkage hypothesis is exerting in theoretical chemistry. It would be an easy matter to name a long list of similar theoretical contributions.

The only hypothesis that offers any explanation for the properties of unsaturated organic compounds is that which supposes the maximum combining capacity of certain of the constituent elements not to be reached. It is obvious, that this is best ascertained by the behavior of the compound toward halogens; but in all cases the constitution of the products must be fully understood before any conclusion should be drawn. The behavior of saturated hydrocarbon towards halogens shows clearly that the affinity which is called a carbon link is not broken in the action of halogens on hydrocarbons. Therefore, when it is found that a compound like ethylene takes up readily two bromine atoms to form symmetrical dibromethene, the only conclusion that can be logically drawn is, that it contained two carbon atoms whose maximum combining capacity is reached by uniting with a bromine atom. Any other inference is without a scientific basis: as that one-fourth of the combining capacity of the carbon was unsaturated, or that the combinations were doubly linked; superfluous and unproven in the first, contradictory to all that is known concerning the union of carbon to carbon in the second.

To return to Demole's last research. It may be well to call attention that a definite proof of oxygen being necessary for the formation of tetrabromethene in the bromine tube has yet to be given. If it were found that when nitrogen is passed through α -dibromethylené, kept at the temperature which the chemical action of oxygen causes the liquid to take, bromacetylene is not formed, or that the latter compound is not formed by keeping α -dibromethylené for a long time at a moderate heat, then a connection may be assumed with some degree of certainty.

VI.—A NEW SYNTHESIS OF ALLANTOIN AND SOME SUGGESTIONS ON THE CONSTITUTION OF URIC ACID.

For reasons, which will be stated below, several attempts were made to obtain mesoxalyldiureide synthetically :

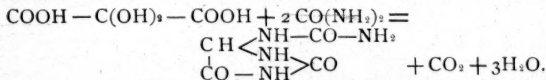


A mixture of equal weights of mesoxalic acid and carbamide was heated in an oil-bath at 110° . An homogeneous liquid was formed, and carbon dioxide given off. After heating several hours the product of the reaction was extracted with boiling water. From the extract prismatic crystals separated on cooling. These were allantoin, as was shown by an analysis and examination of their properties.

0.3555 gram gave 0.3976 gram CO_2 and 0.1248 gram H_2O .

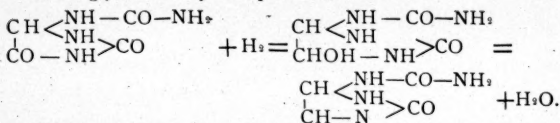
	Theory for $\text{C}_4\text{H}_6\text{N}_4\text{O}_3$.	Found.
C	30.37	30.51
H	3.77	3.90

The formation of allantoin from mesoxalic acid and urea is represented as follows :

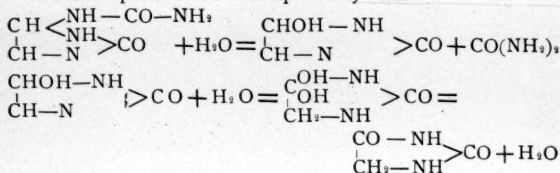


Mesoxalic acid may be heated for some hours at 110° without undergoing a noticeable decomposition, but when heated in presence of other substances it has a great tendency to split off carbon dioxide. An experiment with the same mixture, and using phosphorus trichloride as a dehydrating agent, was next made at a lower temperature (80°). The evolution of carbon dioxide was again observed. From the products of the reaction an amorphous yellow substance was isolated, which did not yield alloxan when heated with nitric acid, and was not further examined. A similar result was obtained by the action of phosphorus trichloride on a mixture of alloxanic acid and carbamide. As oxalylureide is said to be formed by the action of oxalic ether on carbamide, an analogous experiment was made with mesoxalic ether, but no action was observed, either on boiling the mixture in an open vessel, or by heating it in a closed tube.

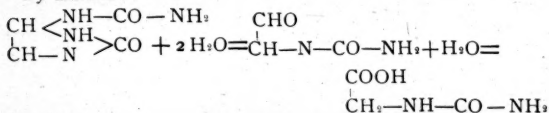
The empirical formula of mesoxalyldiureide, $C_3H_4N_2O_4$, differs from that of uric acid by an additional atom of oxygen. The reduction of uric acid to xanthine needs confirmation,¹ but there can be no doubt that from allantoin a compound containing one atom less of oxygen has been obtained by reduction.² The formation of glycoluril may be represented as follows:



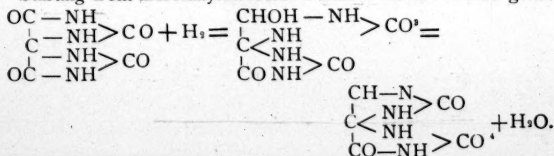
The decomposition of this compound by acids:



By alkalis:



Starting from mesoxalyldiureide a similar reaction would give:



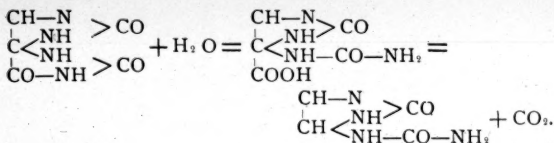
¹ *Annalen der Chemie*, **131**, 121.

² *Ibid.* **134**, 219.

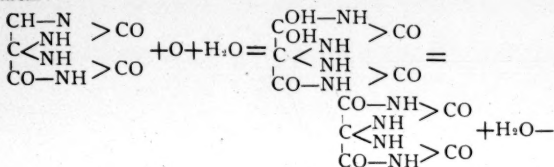
³ The formation of $\text{CO} < \begin{array}{c} \text{NCH}_3 - \text{CHOH} \\ \text{NCH}_3 - \text{CO} \end{array}$ from $\text{CO} < \begin{array}{c} \text{NCH}_3 - \text{CO} \\ \text{NCH}_3 - \text{CO} \end{array}$ by reduction. (Andreasch, *Monatshefte für Chemie*, **3**, 432.)

⁴ The behavior of acetylacetic ether, of malonic ether, and more especially, according to the experiments of Conrad and Guthzeit (*Berichte der deutschen chemischen Gesellschaft*, **14**, 1643; **15**, 2844), of malonylureide towards bases, show that Hill and Mabery's investigation on dimethyluric acid cannot be accepted as conclusively proving that uric acid contains four NH groups.

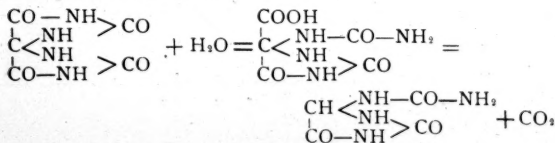
The first product of the decomposition of uric acid by acids should be glycoluril, which, however, would be further decomposed, at the high temperature used in this reaction, into amido-acetic acid, carbon dioxide and ammonia:



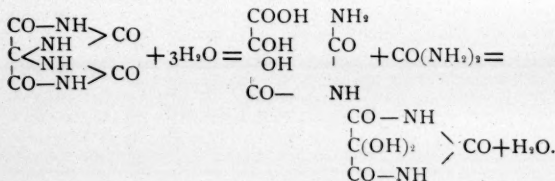
In the presence of oxidising agents an atom of oxygen and water are added, forming the unstable mesoxalyldiureide, which is further decomposed according to the conditions of the experiment:



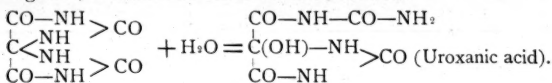
If the oxidation is effected in an alkaline solution this compound decomposes into allantoin.



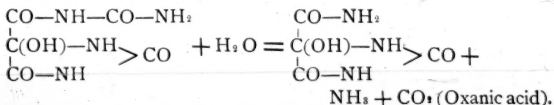
In an acid solution (nitric acid),



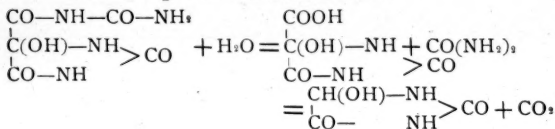
This reaction appears anomalous, but an analogy is found in the conversion of alloxan into oxalylurea by the action of nitric acid. When uric acid in alkaline solution stands exposed in the air for a long time, uroxic and oxanic acids are formed:



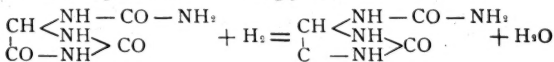
The further action of alkali on this acid:



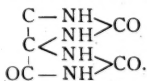
Both these acids go over into allanturic acid:



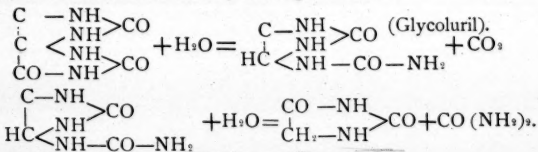
A second possible formula for glycoluril is:



The corresponding formula for uric acid is:



This formula, probably, is more in accordance with the properties of uric acid than the first. It expresses the marked affinity of uric acid for oxygen much more clearly, and equally well the formation of amidoacetic acid by heating with acids:



Perhaps either of these formulæ of uric acid is more strictly based on analogy with the properties and decompositions of the derivatives of uric acid than any as yet proposed; but they would hardly be worthy of publication did they not indicate a possible way to a synthesis of uric acid, which would not fail to throw a strong light on its constitution. Among the numerous experiments that still suggest themselves for the synthesis of mesoxalyldiureide, the action of dibrommalonic acid on the silver derivative of carbamide, or the action of the chloride of that acid on carbamide, may be mentioned.

VII.—ON A CONVENIENT METHOD FOR PREPARING BROMACETIC ACID.

The preparation of bromacetic acid in large quantity by heating acetic acid with bromine in closed tubes is exceedingly tedious, so that the following method, which I and friends to whom it has been communicated have had occasion to use during the past five years, will be found very advantageous. It is based on the decomposition of $(C_2H_3O_2Br)_2 \cdot HBr$ at 100° under ordinary pressure into bromacetic acid and bromhydric acid. Hell and Muhlhäuser,¹ who examined this remarkable compound, attempted to make use of its properties for the preparation of bromacetic acid; but, as they heated it in closed tubes, found the method impracticable on account of the tubes exploding.

A mixture of acetic acid and bromine, in equivalent proportions, and a small amount of carbon disulphide is heated at 100° in a flask with a return cooler until bromhydric acid ceases to be given off. As a small amount of the bromine escapes through the cooler, somewhat more than the theoretical amount may be taken with advantage. It is absolutely necessary, if good results are to be obtained, to use all the reagents in a perfectly anhydrous condition; indeed, on acetic acid containing more than several per cent. of water no action takes place. From the product of the reaction about 90 per cent. of the theoretical amount of bromacetic acid may be obtained by fractional distillation.

Noteworthy is the observation that no dibromacetic acid is formed, even when bromine is used in large excess. Also, that

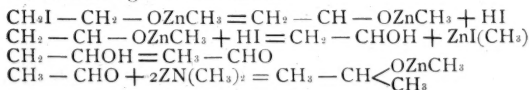
¹ *Berichte der deutschen chemischen Gesellschaft*, **11**, 241.

this method cannot be used for the preparation of brompropionic nor brombutyric acids. It is possible, however, that the acids used in these experiments contained a small quantity of water, which, as is the case with acetic acid, may have prevented the reaction.

VIII.—ON SEVERAL CASES OF INTERMOLECULAR REARRANGEMENT.

It is at present pretty generally understood that what is called intermolecular rearrangement often represents the final step in a series of changes. The consideration of intermolecular rearrangement in this light has shown, in a number of instances, that the intermediate reactions explain the final result.¹

By the action of zinc-methyl on ethylene-iodohydrine, Butlerow and Ossokin² obtained secondary propylalcohol, instead of the primary compound, as was expected. It is possible that this result is due to the previous formation of ethylaldehyde. Wislicenus³ has shown that sodium acts on monochloroacetal to form $\text{CH}_2 - \text{CH} - \text{O} - \text{C}_2\text{H}_5$, and that this compound, on decomposition by dilute sulphuric acid, gives ethylaldehyde and alcohol. According to Butlerow and Ossokin, the first product of the action of zinc-methyl is $\text{CH}_2\text{I} - \text{CH}_2 - \text{OZnCH}_3$, and this compound, heated to a high temperature with an excess of zinc-methyl, gives $\text{CH}_3 - \text{CH} < \begin{smallmatrix} \text{OZnCH}_3 \\ \text{CH}_3 \end{smallmatrix}$. The following equations may represent the various stages of this reaction:



Anschiuetz⁴ has observed that a trace of iodine heated with ethyl malate suffices to convert the compound into ethyl fumarate. The formation of fumaric ether is probably preceded by that of a trace of iodohydric acid, which unites with an equal number of molecules

¹ As is the case in the conversion of dimethylaniline chlorhydrate into the salt of amidodimethylbenzene. (This Journal, **1**, 420; Berichte der deutschen chemischen Gesellschaft, **13**, 2108.) It is much to be hoped that the use of the phrase "atomic migration," which is a misnomer and unscientific, will be discontinued.

² Annalen der Chemie, **145**, 257.

³ Ibid. **192**, 106.

⁴ Berichte, **12**, 2282.

of ethyl malate, forming ethyl iodosuccinate. The interesting experiments of Fittig¹ on the behavior of fumaric and maleic acids towards bromhydric acid, have shown that maleic acid combines much more readily with it than fumaric acid does; in other words, it has a stronger affinity for it. Now, bromsuccinic acid decomposes when heated above its melting-point into fumaric and bromhydric acids, and this decomposition can but take place more easily when a substance like maleic acid, having a strong affinity for bromhydric acid, is present. The conversion of maleic ether into fumaric ether may therefore be considered as the final result of a series of additions of iodohydric acid to ethyl malate and decompositions of the ethyl iodosuccinate into fumaric ether and iodohydric acid.

One of the most remarkable cases of intermolecular rearrangement is the conversion of hydrazobenzene into two isomeric diamidodiphenyls by the action of dilute mineral acids. This reaction is probably intimately connected with the marked tendency of the weak basic —NH—NH— group to take up hydrogen and pass over into strong basic amido groups; thus, hydrazobenzene, when heated, decomposes into aniline and azobenzene. The primary action of chlorhydric acid on hydrazobenzene is to form an unstable salt, probably $\text{C}_6\text{H}_5\text{—NHHC}\overset{\cdot}{\text{I}}$. The salt is then decomposed into $\text{C}_6\text{H}_5\text{NH}_2$ and Cl , and the chlorine acts on one of the hydrogen of C_6H_5 , forming $\text{C}_6\text{H}_4\text{—NH}_2\text{HCl}$, two molecules of which go over into $\text{C}_6\text{H}_4\text{NH}_2\text{HCl}$. It is more likely that the two reactions occur simultaneously, and it is not only a consequence of the affinity of the NH—NH group for hydrogen, but also of chlorine for the hydrogen of the phenyl group. The formation of two isomeric diamidodiphenyls is due to the chlorine acting on hydrogen atoms in the ortho and para-positions toward the NH group.

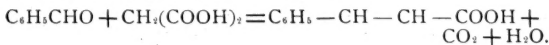
V. Meyer has recently shown that nitrous acid acts on the hydrogen of a methylene group, when the carbon is united with certain negative radicals, replacing it by N—(OH) . This observation may be used to explain the action of nitrous acid on primary amines. The first product of the action of nitrous acid on aniline nitrate should be $\text{C}_6\text{H}_5\text{—N} \begin{smallmatrix} \text{H} > < \end{smallmatrix} \text{N} \begin{smallmatrix} \text{N(OH)} \\ \text{ONO}_2 \end{smallmatrix}$, but the compound $\text{C}_6\text{H}_5\text{—N—N(OH)}$ has not the property of combining with

¹ Annalen der Chemie, **180**, 88; **188**, 91.

acids to form a substituted ammonium salt, a decomposition into $C_6H_5 - N - N(OH)$ and nitric acid therefore takes place. Diazobenzene behaves, however, toward acids like a strong base; the nitric acid, therefore, reacts on it, forming diazobenzenenitrate and water. In the paraffin series the reaction is probably of the same nature, only the instability of the new product is so great that a decomposition into an alcohol and nitrogen takes place at ordinary temperature. This is in accordance with the greater affinity of unsaturated carbon for elements than saturated carbon for the same elements. If $CH_2 - CHNH_2$ were known, it would probably yield a diazo compound that could be isolated.

IX.—ON A NEW SYNTHESIS OF CINNAMIC ACID.

Several years ago¹ I showed that by heating mixtures of benzoic, salicylic or cuminic aldehydes with sodium acetate and phenylacetic acid, stilbene and substituted stilbenes can be obtained. From succinic acid and benzoic aldehyde a well-defined product could not be obtained. Recently this reaction has been tried with malonic acid. A mixture of malonic acid, benzoic aldehyde, in proportion of their molecular weights, and $\frac{1}{2}$ part fused sodium acetate, heated in a closed tube for several hours at 140° , gave a very good yield of cinnamic acid:



It is not necessary, however, to add sodium acetate to the mixture. Benzoic aldehyde and malonic acid, heated for several hours in a closed tube at 130° , gave a satisfactory yield of cinnamic acid. Fittig² infers from the results of his recent experiments on the action of benzoic aldehyde on sodium succinate and acetic anhydride, that in Perkins' reaction the condensation, or carbon-polymerisation, occurs between the salt and the aldehyde, and not between the anhydride and the aldehyde, as was formerly supposed. It seems to me that his results do not permit such a generalisation. It is extremely probable that the product of the action of acetic anhydride on sodium succinate contains, according

¹ This Journal, **1**, 312.

² Annalen der Chemie, **216**, 115.

to the conditions, either a mixed succinic-acetic anhydride, or a mixture of acetic and succinic anhydrides, sodium acetate and succinate. The aldehyde will act on the hydrocarbon group whose hydrogen are the most exposed to the loosening influence of oxygen; in the present instance undoubtedly the methylene of succinic anhydride. Halogens act with difficulty on acetic acid, readily on acetic anhydride; the latter compound is used in Perkins' reaction, whereas the first cannot be used. The reason of the greater reactive properties of the hydrogen of acetic anhydride is to be sought in loosening effect of oxygen on the affinity of carbon for hydrogen. In acetic acid the influence of oxygen has been, in comparison with the anhydride, partly neutralised by a partial replacement of oxygen by hydrogen. In sodium acetate the loosening influence of oxygen is again decreased, in comparison with acetic acid, owing to the introduction of a more positive element in the place of hydrogen; this is exactly the reverse of what Fittig infers from his results. The experiments of this chemist on the action of benzoic aldehyde, acetic anhydride and sodium malonate, do not prove his views. If the mixed anhydride $\text{CH}_2 \begin{matrix} \text{CO-O-OCCH}_3 \\ \text{CO-O-OCCH}_3 \end{matrix}$ is formed, it is evident that the reaction will take place between the CH_2 group and formyl; not to mention that, as the above-described experiment shows, if the affinity of hydrogen for carbon is sufficiently loosened the action of heat alone suffices to effect a condensation. I do not intend to enter into the application of these views to the results of Perkin's, Ogliastro's, Fittig's, and my own experiments; but they offer an explanation for the apparently contradictory results, to which Fittig and others have already called attention. The influence of the oxygen on the properties of organic compounds containing it has not had the general consideration which the subject merits. I shall reserve the theoretical consideration of this subject, as well as the description of a series of experiments now in progress, for a separate paper; and only mention here that it offers a satisfactory explanation for the general form which Gabriel and myself¹ have given to Markownikoff's rule, for Popoff's rule for the oxidation of ketones, and for other equally important facts.

TUFTS COLLEGE, MASS., June 20th, 1883.

¹ Berichte der deutschen chemischen Gesellschaft, **11**, 1016.

ESTIMATION OF SULPHUR IN ORGANIC COMPOUNDS.

BY E. H. KEISER.

Of the many methods devised for the estimation of sulphur in organic substances, Liebig's process for non-volatile compounds is the simplest and most expeditious. As ordinarily carried out, 20-25 grams of potassium hydroxide and 4-5 grams of potassium nitrate are fused in a silver crucible or dish. The fused mass is allowed to cool and a weighed quantity of the substance added. The crucible is then heated, and the contents stirred with a silver spatula until all the carbon is oxidised and the fused mass becomes perfectly transparent. After cooling it is dissolved in water, the solution acidified with hydrochloric acid, and the sulphuric acid precipitated with barium chloride. The weight of barium sulphate thus obtained is generally too high, and it is necessary to purify it by reprecipitation. The chief source of error by this method is due to the fact that the fused potassium hydroxide and nitrate take up an appreciable quantity of silver from the dish or crucible, and, on acidifying with hydrochloric acid, the silver chloride formed is held in solution by the excess of potassium chloride present, and is then carried down by the barium sulphate, thus increasing the weight of the precipitate.

Various attempts have been made to improve the method. Potassium hydroxide alone has been used to fuse the substance with, and the solution treated with bromine to complete the oxidation.¹ But even in this case the fused hydroxide takes up silver, which is afterwards converted into bromide and carried down by the barium sulphate. Besides, certain compounds, such as naphthalene-sulphamide, are oxidised only very slowly by fused potassium hydroxide, and for complete oxidation by this method require protracted heating with a large quantity of alkali.

Accurate results may be obtained, without reprecipitating the barium sulphate, by the following modification of Liebig's method:

Ten grams of caustic potassa, free from sulphur, are fused in the silver crucible and allowed to cool. The weighed substance (0.1-0.3 gram) is then added, and the crucible heated until the

¹ Fahlberg and Iles. *Berichte der deutschen chemischen Gesellschaft*, **11**, 1187.

contents have become thoroughly mixed. One gram of the crystallised potassium nitrate is then added and the heating continued until the fused mass has become perfectly transparent. The crucible is allowed to cool and the contents dissolved in distilled water. The solution is neutralised with hydrochloric acid. It becomes perfectly clear, but if allowed to become cold and then be diluted with a large volume of water ($\frac{3}{4}$ —1 litre), all the silver chloride is precipitated. After allowing the precipitate to settle the solution is filtered, and in the filtrate the sulphuric acid is determined in the usual way by precipitation with barium chloride. The following results were obtained by this method:

I. 0.2556 gram sulphamine-metatoluic acid gave 0.2775 gram BaSO_4 = 14.90 per cent. sulphur.

II. 0.1045 gram sulphamine-metatoluic acid gave 0.1127 gram BaSO_4 = 14.81 per cent. sulphur.

III. 0.1847 gram of sulphamine-metatoluic acid gave 0.1990 gram BaSO_4 = 14.78 per cent. sulphur.

Calculated for $\text{C}_8\text{H}_9\text{SNO}_4$.

S	14.88	Found.		
		I.	II.	III.
		14.90	14.81	14.88

IV. 0.2111 gram β -naphthalene-sulphamide gave 0.2364 gram BaSO_4 = 15.38 per cent. sulphur.

V. 0.1371 gram β -naphthalene-sulphamide gave 0.1547 gram BaSO_4 = 15.49 per cent. sulphur. Calculated for $\text{C}_{10}\text{H}_7\text{SNO}_2$ 15.46 per cent.

S	15.46	Found.	
		IV.	V.
		15.38	15.49

VI. 0.1396 gram taurine gave 0.2611 gram BaSO_4 = 25.67 per cent. sulphur. Calculated 25.60 per cent. sulphur for $\text{C}_2\text{H}_7\text{NSO}_3$.

VII. 0.2464 gram para-dipropyl-benzene-sulphamide gave 0.2399 gram BaSO_4 = 13.37 per cent. sulphur. The formula requires 13.27 per cent.

VIII. 0.2852 gram para-propyl-sulphamine benzoic acid gave 0.2773 gram BaSO_4 = 13.35 per cent. sulphur. The formula $\text{C}_{10}\text{H}_{13}\text{NSO}_4$ requires 13.17 per cent. sulphur.

Dr. W. C. Day obtained by this method the following results:

I. 0.2138 gram cymene-sulphamide gave 0.2304 gram BaSO_4 = 14.79 per cent. sulphur.

II. 0.2824 gram cymene-sulphamide gave 0.3045 gram BaSO_4 = 14.80 per cent. sulphur. The formula $\text{C}_{10}\text{H}_{13}\text{NSO}_3$ requires 15.02 per cent. sulphur.

Communications from the Chemical Laboratory of Rutgers College.

X.—AMMONIUM FERROUS SULPHATE AS A REAGENT FOR NITRIC ACID.

BY PETER T. AUSTEN AND J. CHESTER CHAMBERLAIN.

The easy oxidisability of ferrous sulphate renders it impossible to keep a solution of it as a laboratory reagent; and although methods have been suggested for preserving it—as, for instance, covering the surface with a layer of petroleum—the solution is still generally made only when it is needed.

A solution of ammonium ferrous sulphate, which can now be easily obtained, answers excellently in place of the ferrous sulphate, and has the advantage of being permanent, so that it can be used as a desk reagent. A solution of convenient strength can be made by dissolving 200 grams of the double salt in a litre of water containing about 20 cc. of concentrated sulphuric acid. The solution can easily be made, when the double salt is not obtainable, by dissolving one molecule of ferrous sulphate and one molecule of ammonium sulphate in water containing one or two per cent. by volume of concentrated sulphuric acid. Sufficient amounts of the salts are taken to give a solution containing about twenty per cent. of the double salt.

A convenient solution is made by dissolving 12 grams of ferrous sulphate and 6 grams of ammonium sulphate in 100 cc. of water containing 2 cc. of concentrated sulphuric acid. A slight excess of sulphuric acid seems to have a beneficial effect in making the solution keep. A solution of this kind, after standing in a closed bottle for three months, gave the test with sharpness, and three weeks' exposure in a loosely-covered wide beaker did not injure its powers.

A series of experiments was made to ascertain if the double salt was as delicate a test as the ferrous sulphate alone. A solution of potassium nitrate containing 0.001 gram of NO_3 gave a distinct ring at once, while a solution containing 0.0001 gram of NO_3 gave a perceptible ring on standing three hours. These results were, if anything, more delicate than those obtained with ferrous sulphate alone.

NEW BRUNSWICK, N. J.

XI.—THE ANALYSIS OF STANNATE OF SODA.

BY PETER T. AUSTEN.

The usual method of determining the amount of stannic oxide in sodic stannate is by adding dilute sulphuric acid to the hot solution until it is faintly acid, and then filtering off and washing the gelatinous precipitate of stannic hydroxide. The determinations are, as a rule, quite satisfactory, but the precipitate is very gelatinous and slow to wash.

It occurred to me that the precipitation of stannic nitrate by heat might be applied to the analysis of stannate, and that, as the liquid in this case is strongly acid, the filtration and washing would be easier. It was found that when stannate of soda was acidified with strong nitric acid, a clear solution was obtained from which, when heated to boiling, all the tin was precipitated. In no case could a trace of tin be detected in the filtrate by hydrogen sulphide. The precipitate is flocculent and gelatinous, but not quite so much so as the precipitate of stannic hydroxide obtained by acidifying a solution of the stannate.

The precipitate formed on heating a stannic nitrate solution is insoluble in nitric acid. It is soluble in concentrated chlorhydric acid, and the precipitate formed by adding potassium carbonate to this solution is not redissolved in excess. From this it is to be inferred that the precipitate is metastannic acid, and not stannic hydroxide, as generally stated.

The precipitate is more easily filtered and washed than that of stannic hydroxide. In the following analyses commercial liquid stannate of soda was used. The weighed portion was washed into a beaker with water, using about 25 cc. Concentrated nitric acid was then added drop by drop, while shaking, till a clear solution was obtained. The solution was diluted to about 250 cc. and heated to boiling. After the precipitate had formed, the liquid was well stirred and then allowed to settle. The clear liquid was decanted on a filter, and the precipitate washed a few times with hot water by decantation, then transferred to the paper, and the washing continued until the washings were free from acidity by test paper. The paper and precipitate were dried, incinerated and

heated for two or three minutes over the blast-lamp. Solid stannate of soda is analysed in the same way, a water solution of it being made in the usual manner.

Weight Taken.	Per cent. of SnO_2 .
6.2122	8.94
5.0531	8.92
7.0162	8.91
By precipitation with dil. sulphuric acid.	
6.0822	9.08 ¹
6.6032	8.95

NEW BRUNSWICK, N. J.

REVIEWS AND REPORTS.

ANALYTICAL CHEMISTRY.

*A new method of estimating the Halogens in Volatile Organic Compounds.*² The method now almost exclusively employed for estimating the halogens in organic compounds is that of Carius, which consists in heating the substance in a sealed tube with fuming nitric acid and silver nitrate. R. T. Plimpton and E. E. Graves propose a substitute for this, in the case of volatile compounds. The substance is introduced into a U tube through which illuminating gas and air are passed, as in a Bunsen burner. The volatile substance evaporates and burns with the gas at a tip on one end of the tube, the halogens being left partly free and partly in combination with hydrogen. The evaporation is sometimes aided by warming the tube with hot water, or otherwise. The temperature is raised or lowered so that the substance may always be detected in the flame, and yet not in sufficient quantity to make the flame luminous. The products of combustion are aspirated through a bent funnel tube and collected in dilute caustic soda; this is boiled with sulphurous acid to reduce chlorates, etc., and then the halogens precipitated with silver nitrate. The success of the experiment depends upon the regular volatilisation of the compound; if this is unduly hurried the flame becomes luminous, and the combustion may be incomplete. On the other hand, the evaporation

¹ This precipitate was not quite washed out.

² Journal of the Chemical Society, March, 1883, 119.

should not be too slow, or, before it is complete, the caustic soda in the absorbing tubes will become saturated with carbonic acid.

Hydrogen dioxide in Analytical Chemistry. The discovery of the valuable disinfectant properties of hydrogen dioxide has led to its manufacture on the large scale. It is now sold in the form of a 2—3 per cent. solution in water. A few preliminary experiments have shown that this solution is a powerful and convenient oxidising agent, which must replace nitric acid, bromine and chlorine to a considerable extent, and its use has also been proposed in the larger bleaching industries. A. Classen and O. Bauer¹ now call attention to a scheme by which hydrogen dioxide may be used as a laboratory reagent, particularly in quantitative analysis. The solution just mentioned is not sufficiently pure for analytical purposes; it contains alumina, and, further, is acidified with sulphuric acid, to prevent decomposition, and this would interfere with its use in sulphur determinations. But a solution prepared in Berlin especially for analytical purposes is quite pure, and can be obtained acidified with either hydrochloric or sulphuric acid. It is known that hydrogen dioxide oxidises arsenious acid to arsenic acid, and phosphorous to phosphoric acid; and, further, that it decomposes hydrogen sulphide, forming water and free sulphur,



But the latter reaction does not take place if the hydrogen dioxide acts in *ammoniacal solution*, i. e. on ammonium sulphide. If this substance or sodium sulphide is treated with hydrogen dioxide the liquid becomes warm, and is gradually decolorised without deposition of sulphur. The latter is oxidised to sulphates and hyposulphites. If the liquid is heated, after adding hydrogen dioxide, sulphates alone are formed. By passing hydrogen sulphide through a solution of hydrogen dioxide made strongly alkaline with ammonia, sodium carbonate or caustic potassa, it is completely oxidised to sulphates. No less interesting is the conduct of solutions of sulphides of tin, antimony and arsenic in ammonium sulphide: on adding hydrogen dioxide gradually, the ammonium sulphide is oxidised, causing at first a precipitation of the other sulphides; but by adding an excess of the reagent and heating, tin sulphide is transformed completely into the insoluble oxide, and antimony partly into insoluble oxide and partly into a soluble compound. Arsenic sulphide, however, is transformed completely into salts of arsenic acid. By acting on sulphide of sodium and tin, the latter goes partly or completely into solution, according to the proportion of sulphide of sodium.

The above conduct of hydrogen dioxide towards ammonium sulphide, or the action of hydrogen sulphide gas on ammoniacal hydrogen dioxide, may be applied in qualitative analysis for destroying an excess of these compounds, and in quantitative analysis for

¹ Berichte der deutschen chemischen Gesellschaft, 16, 41061.

determining amounts of gaseous or dissolved hydrogen sulphide, or for the determination of sulphur or metals in sulphides. In cases where the sulphide can be decomposed by the direct action of hydrogen dioxide in presence of ammonia, it is done in this way; in other cases, where heating the sulphide with hydrochloric acid causes the evolution of a definite amount of hydrogen sulphide, the latter is oxidised by hydrogen dioxide and estimated as barium sulphate. Sulphites are likewise completely oxidised to sulphates, and this reaction may be used in several ways for analytical purposes.

The sulphides of arsenic, copper, zinc and thallium are oxidised without the formation of a precipitate. In the case of copper, after the oxidation is complete and the excess of ammonia driven off, the copper is all left as a green insoluble powder which is not altered by ignition; by treating sulphide of zinc in a similar manner only part is obtained as a white precipitate, the rest going into solution. By the action of hydrogen dioxide on antimony trisulphide part of the antimony is precipitated as oxide, but in all these cases the liquid contains all the sulphur as sulphuric acid. Hydrogen dioxide acts in various ways on the other metallic sulphides. It attacks mercury sulphide energetically, although this is hardly changed with nitric acid. After driving off the ammonia the mercury is all found in a spongy precipitate.

Sulphide of cadmium is similarly transformed into a light yellow precipitate, but after complete oxidation a portion of the cadmium is also found in solution as sulphate. Some metallic sulphides, which can be precipitated by ammonia from their solutions in acids, are decomposed by ammoniacal hydrogen dioxide, with the formation of sulphuric acid and precipitation of the metals as hydroxides. Sulphides of iron and manganese are quickly oxidised in this way. By heating cobalt sulphide with ammoniacal hydrogen dioxide, cobalt sulphate is first formed, which is partly converted into a brown precipitate on further heating. Sulphide of nickel yields a green precipitate which does not contain all of the metal. Sulphides of silver and bismuth are not completely decomposed. Sulphide of lead is easily oxidised to sulphate.

With these preliminary statements as to the action of hydrogen dioxide on the metallic sulphides, the following are the analytical processes to which it is applied: The property of oxidising hydrogen sulphide in alkaline solution easily and completely to sulphuric acid, may be taken advantage of in the estimation of chlorine, bromine and iodine in liquids containing hydrogen sulphide. In the case of chlorine an ammoniacal solution of hydrogen dioxide is added to the liquid containing the chloride and hydrogen sulphide, and this is boiled until the complete decomposition of hydrogen dioxide is shown by no more oxygen being evolved. The chlorine is then precipitated with silver nitrate in the usual way. When bromine or iodine is to be determined, the hydrogen dioxide

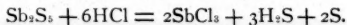
is made alkaline with sodium carbonate. If an ammoniacal solution is used, ammonium nitrite is formed, which is decomposed on acidifying and causes the liberation of free bromine or iodine.

As indicated above, metallic sulphides which are oxidised directly by hydrogen dioxide may be estimated by determining the amount of sulphuric acid formed in the oxidation. This method is applicable for the estimation of arsenic, antimony, zinc, copper and cobalt. The authors have shown by special experiments that all the arsenic is oxidised to arsenic acid, which they determine as ammonium magnesium arsenate. Antimony trisulphide is oxidised completely by hydrogen dioxide, but the pentasulphide is not completely oxidised. The principle of estimating hydrogen sulphide evolved by hydrochloric acid from such metallic sulphides as are decomposed by this means, has been in use for some time, a solution of bromine being used to oxidise the hydrogen sulphide. But the objectionable properties of bromine on the one hand, and the fact that all excess of it, as well as hydrochloric acid, must be gotten rid of before precipitating the sulphuric acid, and further, the frequent precipitation of sulphur during the process, are reasons enough for the use of the hydrogen dioxide solution in its stead, especially as it contains nothing which interferes with the direct precipitation of the sulphuric acid. The estimation of metals by this means is capable of more extended application than the direct oxidation of the sulphide. Pure metallic sulphides are seldom obtained in analyses, but more frequently mixtures with free sulphur.

The estimation of antimony and tin in these mixtures is a difficult matter and always requires considerable time. But the amount of free sulphur does not affect the quantity of hydrogen sulphide liberated by an acid, and hence the advantage of determining the latter. It is absorbed in a peculiar apparatus, described in full by the authors. Foremost among the metals that may be conveniently determined in this way are antimony, tin, cadmium and iron. When antimony trisulphide is treated with hydrochloric acid, under the proper conditions, it yields three molecules of hydrogen sulphide,



Antimony pentasulphide is decomposed with liberation of the same amount of hydrogen sulphide and deposition of sulphur,



As far as the estimation of the antimony is concerned, it is immaterial whether it is in the form of tri- or pentasulphide or a mixture of both, for three molecules of hydrogen sulphide always represent two atoms of antimony.

Sulphites may be determined in the same way as sulphides. If the sulphite is free from sulphate it may be oxidised with hydrogen di-

oxide directly; but if sulphuric acid is present, the sulphurous acid is evolved and then oxidised as usual. The method allows of the estimation of a hyposulphite, sulphite and sulphate in the same liquid. By boiling with an acid the sulphurous acid of the sulphite and hyposulphite is liberated and determined. The sulphur, precipitated from the hyposulphite during this process, is filtered off and weighed, this gives the amount of hyposulphite originally present. Finally the sulphuric acid is precipitated as barium sulphate.

*The Substitution of Ammonium Hyposulphite for Hydrogen Sulphide in the general course of Qualitative Analysis.*¹—A. Orlowsky has found by his investigations on the action of ammonium or sodium hyposulphite on solutions of the ordinary metals, that, 1. All metals that can be precipitated by hydrogen sulphide in acid solutions are also precipitated by ammonium or sodium hyposulphite, from a boiling solution acidified with hydrochloric acid. Lead alone furnishes an exception, inasmuch as it remains in solution together with a portion of the cadmium, if the solution is very acid. 2. The metals thus precipitated may be divided into two classes by means of alkaline sulphides. 3. Metals which are not precipitated by hydrogen sulphide from an acid solution are not precipitated by hyposulphites. 4. The salts of the alkaline earths, however, conduct themselves toward hyposulphites in a manner entirely different from that exhibited with hydrogen sulphide and ammonium sulphide. In neutral or alkaline solutions, hyposulphites of the alkaline earths are formed, which are precipitated from acid solutions by ammonia. By continued boiling the hyposulphites of the alkaline earths are decomposed into sulphates and sulphites. Ammonium or sodium hyposulphite may be used, therefore, for the detection and also for the separation of metals. In applying them to the general course of separation of metals, Orlowsky proceeds as follows: Lead, barium, strontium and part of the calcium, are first separated from the solution by ammonium sulphate, and detected in the ordinary way. The filtrate, which must not contain nitric acid, is acidified with hydrochloric acid and heated to boiling, then it is treated gradually with sodium or ammonium hyposulphite, warming and shaking thoroughly between the additions. The liquid must remain acid to the end of the reaction. The precipitate may contain sulphides of antimony, arsenic, tin, gold, platinum, mercury, silver, copper, bismuth, and cadmium. These may be further treated with ammonium sulphide. The filtrate is neutralised with ammonia and precipitated as usual with ammonium sulphide, by which, however, cadmium may be in the precipitate, and will be found further on with the zinc and manganese. In the last filtrate antimony and tin must be sought for as well as the alkalis and calcium and magnesium,

¹ Journal der russ. phys. chem. Gesellschaft, 1883, 32, and Berichte der deutschen chemischen Gesellschaft, 16, 807.

since these metals like cadmium are not completely precipitated from acid solution by ammonium hyposulphite.

Nitrogen.—As a general method for the determination of nitrogen, H. Gronnen¹ recommends burning the nitrogenous substance in a slow current of superheated steam. The substance is placed in a wrought-iron tube containing fragments of a peculiar kind of clay. This tube is connected with another in which steam is generated; both are enclosed in a peculiar charcoal furnace and heated to bright redness. The nitrogen is all converted into ammonia, which is absorbed and estimated as in soda lime process. The method is applicable for determining nitrogen in food, vegetables containing nitrates, guano and ammoniacal superphosphates, and also for commercial saltpetre. In the latter case sugar is added to the substance, so that carbon will be present to decompose water and liberate hydrogen, with which the nitrogen forms ammonia.

Phosphorus.—The determination of phosphoric acid by the molybdenum method,² by Ernst Täuber. The results of this series of investigations are, in the main, confirmations of the views of Stünkel, Wetzke and Wagner, and Maercker; and are in brief as follows:

1. The presence of large amounts of ammonium nitrate is advantageous when phosphoric acid is precipitated from nitric acid solutions by molybdenum solutions. It hastens the precipitation, renders a great excess of molybdic acid unnecessary, and gives the precipitate a loose, spongy character.

2. The precipitate of ammonium phospho-molybdate may be washed with a solution of ammonium nitrate.

3. Magnesium mixture must be added slowly, with stirring, to the ammoniacal phosphate solution.

4. Igniting the magnesium pyrophosphate with a blast lamp is unnecessary for the usual cases of analysis.

Chromium.—Chalmers Harvey³ proposes a method for the volumetric estimation of chromic acid in chromates and bichromates analogous to his method for the analysis of manganese dioxide.⁴ The chromic acid is reduced by heating with a known amount of stannous chloride in excess, and this excess titrated with a standard solution of ferric chloride. Determinations can be made in a few minutes, and the results given are quite accurate; but a manifest objection to the method is, that the solution of stannous chloride is liable to change; and, further, it is not easy to prepare a solution of ferric chloride free from both ferrous chloride and chlorine.

A New Reaction of Aldehydes.—F. Penzoldt and Emil Fischer⁵ have found that by mixing grape sugar with an alkaline solution of diazobenzene-sulphonic acid a red color is produced after 10–15 minutes, and this gradually changes to a violet. Acetaldehyde

¹ Die landwirthschaftlichen Versuchs-Stationen, **28**, 343.

² Chemical News, **47**, 86.

³ Berichte der deutschen chemischen Gesellschaft, **16**, 657.

⁴ *Ibid.* **28**, 333.

⁵ *Ibid.* **47**, 2.

gives the same reaction, but the color is not produced under the above conditions with the more stable aromatic aldehydes. It may be produced easily, however, by an addition of sodium amalgam. By use of the latter the reaction is also hastened and increased in the case of grape sugar and acetaldehyde. The reaction is so characteristic that it appears particularly adapted for the detection of aldehydes. The test is best conducted with pure crystallised diazobenzene-sulphonic acid. It is dissolved fresh each time in about 60 parts of cold water with a little dilute caustic soda. The substance to be tested is added, mixed with dilute alkali, and then a small piece of sodium amalgam, and allowed to stand quietly. If an aldehyde is present, the reddish violet color, similar to pure fuchsine, appears in 10-20 minutes. The test is much more delicate than the reaction with fuchsine-sulphurous acid. Oil of bitter almonds may be detected with certainty in a dilution of 1 part in 3000. Neither chloral nor benzoin gives the reaction, and acetone and acet-acetic ether give under like conditions a dark red color without the characteristic violet tinge. The same is true with phenol, resorcin, and pyrocatechin, if care is taken to have an excess of alkali present to prevent the formation of the known azo-dyes.

Litmus, methyl-orange, phenacetolin and phenol-phthalein as indicators.—Robert T. Thomson¹ has made a series of comparisons of these indicators for the purpose of determining the relative degree of sensitiveness of which each is capable, both in solutions containing only pure acids or alkalies, and also when various impurities are present. The tests were made in such a way that the solution employed would measure about 100 cc., when the end reaction was observed. The strengths of the indicator solutions were so arranged that equal volumes of each gave about the same intensity of color at the point at which the change, caused by excess of acid or alkali, was just complete. 0.5 cc. was used in each experiment. When no interfering substance was present the indicators all gave quite sharp results, phenol-phthalein requiring somewhat less standard alkali for bringing out its characteristic color than did the others. In determining the alkalinity of caustic soda containing some sodium carbonate, methyl-orange lost somewhat in sharpness, this being due to the presence of the neutral salt formed in the reaction. Phenacetolin may be used to determine the amount of hydroxide and carbonate in commercial caustic soda, but if the proportion of carbonate is considerable the reaction is not sharp. Phenol-phthalein can be used for the above purpose very readily, for it loses its alkaline indication when all the sodium hydroxide has been neutralised and the carbonate converted into acid carbonate. On decomposing the acid carbonate by boiling, the red color reappears, and thus the amount of carbonate may be determined. Phenol-phthalein does not give good indications in

¹ Chemical News, 47, 123, 135, 184.

the presence of ammonium salts. Litmus and phenacetolin are quite as delicate in the presence of sulphates, nitrates and chlorides of sodium, potassium and ammonium. When these salts were tested with the volume of methyl-orange used in the foregoing experiments it was found that about 0.2 cc. of normal acid was required to bring out the full pink color, against 0.05 cc. when distilled water only was employed, although a distinct change was produced in the former case. The delicacy of phenol-phthalein is not affected by the salts of sodium and potassium mentioned above, but quantities of sulphate, nitrate and chloride of ammonium equivalent to 0.85 gram of ammonia per 100 cc., required about 1.5 cc. of normal caustic soda to produce even the faintest red color, showing that ammonia and its salts must be carefully excluded when this indicator is made use of. Sulphites of the alkalies are alkaline with litmus, methyl-orange and phenacetolin, until half the sulphite has been neutralised. Phenol-phthalein is practically neutral with sulphites. With sulphides the liberation of sulphuretted hydrogen, on adding a standard acid, does not affect methyl-orange, but with the other indicators the hydrogen sulphide must be boiled off in order to estimate all of the sulphide. Statements are also made as to the phenomena accompanying the titration of phosphates, silicates, nitrites, borates, oxalic, tartaric, citric, and the ordinary mineral acids.

Phenol-phthalein.—N. Menshutkin¹ has shown that the alkaline reaction of triethylamine with phenol-phthalein is destroyed by alcohol. When water, containing a few drops of phenol-phthalein solution, is treated with triethylamine it is colored purple violet. An aqueous solution of triethylamine shows a strong alkaline reaction. If, now, alcohol is added the color becomes paler, and disappears when two volumes of 95 per cent. alcohol have been added. On the other hand, if phenol-phthalein is added to alcohol, and then triethylamine, there is no violet coloration. The alkalinity of the triethylamine has disappeared. Alcohol destroys the compound of phenol-phthalein with triethylamine, even with a great excess of the latter. The color that has been destroyed by alcohol is restored by the addition of an alkali, but it is not as intense as the aqueous solution. Similarly the color given to phenol-phthalein by ammonia is destroyed by the addition of three volumes of alcohol. The author has used this reaction for distinguishing between ammonia and free alkalies in the same solution.

D. T. D.

¹ Berichte der deutschen chemischen Gesellschaft, **16**, 319.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

(Continued from 4, 468.)

METABOLISM.

Formation of Urea.—The place where urea is formed in the body has been for some time more or less of an open question. Recently W. v. Schroeder¹ has obtained positive results by a series of experiments, in which a current of blood was made to circulate through living organs, the amount of urea in the blood being determined both before and after it had passed through the organ in question. The method employed in the determination of the urea was a somewhat novel one, being a combination of Liebig's and Bunsen's method. 100 cc. of blood were precipitated with five times its volume of absolute alcohol, filtered after standing twelve hours, and the filtrate evaporated to dryness at a temperature not exceeding 75° C. The residue was dissolved in water, and the solution, which filters very slowly, clarified by the addition of a little alum solution and an excess of baryta water, followed by precipitation of the baryta with carbonic acid. The filtrate was precipitated with mercuric nitrate, from which the urea was separated by hydrogen sulphide, and the solution heated in a sealed tube with an ammoniacal solution of barium chloride. The barium carbonate thus obtained was not weighed, but the carbonic acid was liberated by citric acid and then measured. The accuracy of the method was proved by control experiments.

After a preliminary experiment with a dog, which confirmed the accumulation of urea in the blood after extirpation of the kidneys, v. Schroeder made an injection experiment with an ox kidney, in which ammonium carbonate was added to the blood. The content of urea in the blood was not at all increased. Similar experiments with dogs' kidneys led to a like result. Thus, in one experiment the amount of urea in the blood was .0140 per cent. before the injection, while after the injection it was .0137 per cent. In a second experiment the blood before the injection contained .0384 per cent. urea; afterwards, .0372 per cent. It is thus apparent that neither the kidneys nor the muscles, which during the experiments retain their excitability, are capable of converting ammonium carbonate into urea. Further experiments were made with the livers of dead dogs, two always being used, the smaller furnishing the liver, while the blood of both, about one litre, served for the injection. The blood was introduced into the portal vein and taken out from the vena cava above the diaphragm, the hepatic artery being ligatured. In one experiment the entire quantity of blood (1250 cc.) was passed through the liver three times, and then a sample

¹ Archiv f. exp. Path. 15, 364. Also Centralbl. f. med. Wiss. 1883, 84.

taken for analysis. The remaining 1000 cc. were passed through the liver during 3½ hours twenty times, altogether .16 gram of ammonia being added in the form of ammonium carbonate. The blood prior to the injection contained .0442 per cent. urea; after the injection .0812 per cent., while the solid matter had only very slightly increased. In a second experiment the amount of urea increased from .0538 per cent. to .1253 per cent. To guard against the possibility of the blood in its passage through the liver taking up substances other than urea which would furnish carbonic acid by heating, v. Schroeder made an experiment with the liver of a hungry dog, without the addition of ammonium carbonate to the blood. There was no appreciable difference in the content of urea before and after the injection. An increase of urea, however, was noticed when the liver of a dog in full digestion was employed. In this case the content of urea in the blood rose from .0499 per cent. to .0636 per cent. without the addition of ammonium carbonate—that is to say, the liver possesses the power of converting into urea some antecedent substance formed during digestion. In one experiment 1.184 grams of urea were formed during 4 hours. If, therefore, 30–40 litres of blood could pass through the liver of a living dog weighing 15 kilos in one hour, 30–40 grams of urea would be formed during the 24 hours; from which it would appear that the entire quantity of urea excreted during one day could be formed in the liver. Regarding the theory of its formation, v. Schroeder holds that the ammonium carbonate passes directly into urea by a withdrawal of water.

Further contributions to our knowledge concerning the formation of urea have been recently made by E. Salkowski,¹ who has studied the behavior of several amido acids in the animal body. Amidobenzoic acid was first studied with a view to ascertain whether it passed into uramidobenzoic acid in the organism, an idea contradictory to the earlier researches of Schultzen and Graebe,² according to whom the amidobenzoic acid should form amidohippuric acid. In his experiments Salkowski used metamidobenzoic acid, which was given to rabbits and dogs in quantities of 2 to 10 grams per day in the form of a sodium salt. In the urine uramidobenzoic was found in sufficient quantity for analysis and to thoroughly establish its identity. In the case of rabbits 5 per cent. was obtained as uramidobenzoic acid, and in the case of dogs nearly 20 per cent. Thus by carnivorous as well as by herbivorous animals, and also by the human body, a definite quantity of uramidobenzoic acid is formed from amidobenzoic, thus furnishing a new example for the addition of cyanic acid to those already known in the body; since as yet, under the conditions which prevail in the animal organism, no other mode of formation of uramido acids is known than the addition of cyanic acid. For the herbivorous animals,

¹ Zeitschrift für physiologische Chemie.

² Annalen d. Chem. u. Pharm. 142, 354. See this Journal, 2, 270.

as Salkowski¹ remarks, this fact is not without value. This investigator had previously shown the formation of uramidobenzoic acid by rabbits, and for a long time this remained the only example of uramido acid formation by herbivorous animals, until Blendermann² proved the addition of cyanic acid to tyrosin in the rabbit. From the observations of Jaarsveld and Stokvis,³ and even more from those of Schmiederberg⁴ on the decomposition of hippuric acid in the body, it might be supposed that a considerable quantity of uramidobenzoic would be formed, not however to be excreted as such, but further decomposed. Against the correctness of this latter view Salkowski finds that even small quantities of uramidobenzoic acid introduced into the body are found again in the urine. Again, Salkowski has endeavored to ascertain, by feeding experiments on dogs and rabbits, the influence of amidobenzoic acid on proteid metabolism. His results tend to show that the excretion of urea is increased under the influence of this acid, but at the same time a larger quantity of albumin is decomposed, which furnishes the necessary amount of nitrogen for the formation of uramidobenzoic acid. The production of urea is, however, not dependent on the formation of the latter acid; it goes on quite independent of this. In regard to where uramidobenzoic acid is formed, Salkowski found that after extirpation of the kidneys of a rabbit, the acid was present in the blood, liver and muscles, after amidobenzoic acid had been given. After ligaturing the ureters, the amount of acid found in the organs was not increased, so that it is plainly apparent that the formation of uramidobenzoic acid does not take place in the kidneys; and since v. Schroeder has found that the change from ammonium carbonate to urea takes place in the liver, it is quite probable that the former change also takes place there.

There are now, as Salkowski remarks, four amido acids, viz. sarcosine, taurine, tyrosine and amidobenzoic, which illustrate the formation of uramido acids. These substances appear in the urine partly as uramido acids and partly as anhydrides. Only a portion of the substance is concerned in the reaction, and the behavior of the individual amido acids is exceedingly variable, being probably dependent upon the behavior of this residue. Thus as decomposition products of tyrosine Brieger⁵ has discovered phenol, Blendermann⁶ oxyhydroparacumaric acid and tyrosinehydantoin, Schultzen and Nencki even urea. Taurine likewise, as Salkowski has shown, behaves in a similarly complicated manner. In the human body and in dogs, only uramidoisethionic acid and unaltered taurine are discovered; but in rabbits, taurine when introduced into the intestines is decomposed into thiosulphuric acid, sulphuric acid and urea. The amido acids of the fatty acid series,

¹ *Zeitschrift für physiologische Chemie*, **1**, 31.

² *Archiv f. exp. Patholog.* **10**, 268.

³ *Zeitschrift für physiologische Chemie*, **2**, 256.

⁴ *Ibid.* **6**, 234.

⁵ *Ibid.* **14**, 379.

⁶ *Ibid.* **6**, 234.

$C_nH_{2n}O_n$, decompose, so far as is known, either wholly or in great part, with formation of urea, only a small portion being excreted unchanged. Salkowski does not agree with Schiffer's¹ belief that the greater part of the sarcosine is excreted unchanged, only about one-fifth being converted into the corresponding uramido acid or anhydride, but considers that the greater part of the sarcosine is excreted in the form of urea; this as a result of experiments on rabbits.² From experiments on dogs Salkowski was led to the same conclusion, viz. that glycocoll is in great part changed into urea, a small portion only being excreted unchanged; that sarcosine behaves in a similar manner, the only point of difference being that the portion excreted unchanged is somewhat larger. The formation of urea in the organism, however, is not dependent on the formation of uramido acids, and the uramidobenzoic acid is not formed from the food of the urea.

Chemistry of the Cell Nucleus and its relation to Urea.—It has long been a recognised fact that there is a quantitative relationship, inside the living organism, between phosphoric acid on the one hand and nitrogenous substances on the other. In the vegetable kingdom it has been observed that, in the upbuilding of nitrogenous tissue, there is also an increase of phosphoric acid in the tissue in question. In the animal kingdom, quantitative examinations of the excretory products have led to like results. In the urine of a hungry animal containing a definite quantity of nitrogen there is always found a relative quantity of phosphoric acid. Again, when more nitrogen is taken in the food than appears in the urine, the amount of phosphoric acid found in the excrement is less than that taken in the food, from all of which Kossel³ infers the possibility of a compound of albuminous matter with certain phosphates or phosphoric acid. As the nearest approach to such a combination we have the nucleins. Their widespread distribution and their relation to the cell nucleus make their metabolism of particular interest. Previous experiments of Kossel⁴ have shown that the chemical composition of nuclein is peculiar, and that it is by itself sufficient to explain the above-mentioned appearances. Among its decomposition products is a body which has approximately the composition of albumin, and which furnishes the same decomposition products as the latter, viz. leucine, tyrosine, indol, etc. Such a substance, a compound which, together with phosphoric acid, contains an albuminous-like molecule, has long had an hypothetical existence, as it alone could explain the quantitative relations between the tissue-forming material. The quantitative determination of nuclein presents many difficulties. Kossel, however, has attempted it, estimating not the nuclein itself, but the nuclein-phosphoric acid. Following are a few of the results showing that the quantity of nuclein in the various organs is not inconsiderable.

¹ Zeitschrift für physiologische Chemie, **5**, 266.

² *Ibid.* **4**, 107-121, also page 124.

³ Zur Chemie des Zellkerns. A. Kossel, Zeitschrift f. physiolog. Chem. **7**, 7.

⁴ Zeitschrift f. physiolog. Chem. **3**, 284. *Ibid.* **4**, 290.

Percentage of Nuclein-Phosphoric Acid in Moist Tissue.

Spleen from horse, .867	Brain from sheep, .313
Spleen " ox, .636	Muscle " ox, .092
Liver " dog, .444	Muscle " ox embryo, .149
Liver " ox, .390	Blood, human, trace
Pancreas " ox, .580	Blood " in leukaemia, .286
Kidney " ox, .285	Pus, " .154

The proof that the phosphoric acid figures correspond to the content of nuclein in the various organs is to be found in the fact that the organs containing the most cell nuclei (spleen, liver and pancreas) yield much more nuclein-phosphoric acid than the tissue poor in nuclei (blood and muscle). Again, the difference is quite striking in the case of normal blood and leukaemic blood, also in the comparison of developed muscle with the embryonic muscle rich in nuclei.

In addition to the phosphoric acid Kossel likewise determined in several cases the characteristic decomposition products of nuclein, viz. guanine, xanthine and hypoxanthine. It has been suggested that the amount of these latter bodies might be made to serve as an index of the amount of nuclein, but that this view is untenable is manifest from the varying proportion of hypoxanthine found. For while in many of the organs the quantity of hypoxanthine is in proportion to the quantity of nuclein, in the muscles it is not the case. Thus in the muscles of the hen the content of nuclein is extremely small, while the content of hypoxanthine is excessive.

Kossel also calls attention to the fact that there are two so-called nucleins (those from cow's milk and the yolk of egg) which, on decomposition, fail to yield either xanthine, hypoxanthine or guanine, and, in this respect at least, as well as in not coming from cell nuclei, differ from the nuclein present in living tissues. Again, as Kossel points out, his quantitative results show plainly that those organs to which we ascribe special activity, as in the nutritive and regenerative processes of the animal body, liver and spleen for example, contain far more phosphoric acid in the form of nuclein than the locomotor apparatus. A study was likewise made of the proportion of nuclein in the liver and muscle of hens at different stages of digestion, and at the same time xanthine and hypoxanthine were determined together with total nitrogen and solids. Following are the results in percentage of the moist tissue.

	Liver.		Breast muscle.	
	Hungry.	Fed.	Hungry.	Fed.
Nuclein-phosphoric acid	.511	.264	.150	.111
Solids	29.500	39.500	27.400	27.000
Nitrogen	4.250	4.410	4.450	4.410
Xanthine	...	...	.038	.011
Hypoxanthine	...	...	.073	.129

As is seen from the table, the content of nuclein-phosphoric acid is not noticeably different in the muscle under the different conditions, while in the liver a decided difference is noticed. From this it is apparent that the nuclein-phosphoric acid during the condition of hunger is less readily withdrawn from the tissue than the remaining phosphoric acid compounds. Plainly the results afford no evidence whether in the tissue of such organisms as are forced to live upon their own tissue, a decomposition of nuclein takes place. In the attempt to settle this point Kossel made several experiments, which led him to the belief that nuclein cannot be considered as a "reserve fund" upon which the organism can live, for, as he remarks, the quantity of nuclein varies but little either in hunger or in full digestion. The physiological function of the nuclein is rather to be sought for in relation to the formation of new cells in the upbuilding of the tissue. A comparison of the nuclein content of a rapidly developing embryonal muscle, with that of a fully developed one, lends favor to this view.

While from previous experiments Kossel had found that both xanthine and hypoxanthine were formed from nuclein, guanine, which by the action of nitric acid is changed into xanthine, has likewise been proved to be a decomposition product of nuclein. In this connection it is well to remember that guanine through oxidation yields guanidine, and this in turn urea; thus by bringing these bodies into genetical relationship we have a series, the two end members of which are on the one hand urea, on the other the cell nucleus. The production of urea from guanine in the organism has, as Kossel remarks, been plainly demonstrated by the feeding experiments of Kerner.¹ Again, in support of a possible production of uric acid from hypoxanthine, we have the fact that the muscles of such organisms as excrete uric acid as the chief product of their metabolism are much richer in hypoxanthine than those of man or the horse. As another support to this view there is the fact that in leukaemia, where the nitrogenous bases of blood, guanine, xanthine and hypoxanthine, are greatly increased, which Kossel deems due to the increased number of cell nuclei, the quantity of uric acid excreted is likewise greater.

Kossel has repeated Demant's² experiments regarding the behavior of these three nitrogenous bases under the various physiological conditions of the body, and has found, contrary to Demant's results, only a slight diminution of hypoxanthine in the hungry condition, as is seen from the foregoing table. From an examination of the liver, spleen and blood in a case of leukaemia, Kossel found that the amount of hypoxanthine in the two former organs was not essentially different from the amount normally present, while in the blood the amount was greatly in excess of the normal quantity. Accepting the view that the cell nucleus is the mother-substance of hypoxanthine, we should naturally expect a change in the percent-

¹ *Annalen der Chemie*, **103**, 249.

² *Zeitschrift für physiologische Chemie*, **3**, 381.

age amount of hypoxanthine in those places where the white nucleated blood corpuscles appear in the place of the red corpuscles; but little or no change in those organs where, in consequence of the leukaemic disease, nucleated cells of the normal organ are displaced by nucleated cells of pathological origin. Hence the above percentages of hypoxanthine in leukaemia are such as would be expected in view of the origin of the base in nuclein.

R. H. CHITTENDEN.

ON THE DIFFERENT MODIFICATIONS OF SILVER BROMIDE AND SILVER CHLORIDE.

Hermann W. Vogel has made a comparative study of the properties of silver bromide, obtained by precipitation in an aqueous solution of gelatin, and those of the same compound prepared by precipitation in an alcoholic solution of collodion. In 1874 Stas called attention to six modifications of silver bromide. One of these, granular bromide of silver, obtained by boiling the flocculent precipitate for several days with water, he stated was the most sensitive to light of all substances known; exposure for two or three seconds to the pale blue flame of a Bunsen burner being sufficient to blacken it. Important as this fact was for photographers it was not applied for years, and it was only in 1878 when, it having been found that silver bromide precipitated in a gelatin solution and boiled for several hours becomes much more sensitive to light, that the remarks of Stas were recalled. To-day these observations have become of the greatest importance to practical photography. They have led to the preparation of the silver bromide gelatin emulsion and the silver bromide gelatin plates, which are twenty times more sensitive than the silver iodide collodion plates, and have become indispensable when impressions are to be taken in a dim light.

The extraordinary sensitiveness of silver bromide in gelatin seemed the more remarkable since it was known that silver bromide in collodion is only moderately sensitive. The explanation was sought for in various directions, but as the result of numerous investigations it appears that the chief cause of the difference is the presence of different modifications of silver bromide. From a consideration of the work already done on the subject, Vogel suspected that silver bromide precipitated in an aqueous colloidal liquid would have notably different properties from silver bromide precipitated in an alcoholic colloidal solution. Silver bromide was prepared in many different ways. Emulsions were made in bromide solutions containing gelatin or collodion (the former aqueous, the latter alcoholic), some with the aid of heat, others without. Part of the emulsion was then poured upon plates kept at a moderate temperature and dried. The remainder was boiled or treated with ammonia before being applied to the plates. He also precipitated silver bromide in dilute gelatin or collodion

solutions, allowed it to settle completely, washed the precipitate, and mixed it with a new portion of gelatin or collodion before applying it to the plates. Finally he precipitated pure silver bromide, in the absence of all colloids, by means of pure aqueous or alcoholic solutions of bromides and attempted to bring this upon plates, using gelatin or collodion as a cement. The result of all these experiments is that there are essentially two modifications of silver bromide, the one being obtained by precipitation in aqueous, the other in alcoholic solutions. The first, on account of the position of the maximum of sensitiveness for the solar spectrum, he calls blue sensitive, the other for the same reason indigo sensitive.

It is of no consequence whether the aqueous or alcoholic solution in which the silver bromide is formed contains gelatin or collodion, or whether the precipitation is effected with excess of bromide or of silver nitrate. It makes no difference whether the solution is hot or cold, or whether the silver bromide is treated with ammonia or whether it is boiled or not. The only necessary condition is that in precipitating indigo sensitive silver bromide the solutions must contain at least 96 per cent. of alcohol. From aqueous alcoholic solutions blue sensitive silver bromide is precipitated.

Besides the difference of sensitiveness towards the solar spectrum, these modifications of silver bromide exhibit other characteristic differences in properties which indicate beyond a doubt that they are two essentially different modifications of the same substance. Among these are, 1st. Their unequal divisibility in gelatin or collodion solutions. The indigo sensitive silver bromide cannot be distributed through a gelatin solution, while the blue sensitive modification does so very readily. 2d. Their unequal reducibility; the blue sensitive silver bromide being reduced with much greater difficulty than the indigo sensitive variety. 3d. Their different action toward chemical and physical sensitizers. 4th. Their different action toward photographic developers. 5th. Their different action under the influence of heat. The blue sensitive variety if heated under water has its sensitiveness perceptibly increased, while the other is not changed by such treatment.

A direct transformation of one modification into the other has not yet been accomplished. The effect of the light upon these substances is incipient reduction, and we might hence suppose that the more easily reducible indigo sensitive variety would be the more sensitive to light. But this is not the case, because it is not chemical reducibility, but the absorption power for light that is of the greatest importance. Now the blue sensitive silver bromide has a greater absorption power than the indigo sensitive variety, and hence its greater sensitiveness. Silver chloride prepared by methods similar to those used in making the two forms of bromides was also found to exist in two modifications. One is designated as ultra violet sensitive, the other as violet sensitive silver chloride.—(*Berichte der deutschen chemischen Gesellschaft*, 16, 1170.) E. H. K.